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The mechanism of adsorption at the interfaces of dilute sodium oleate solutions.

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MECHANISM OF ADSORPTION AT THE INTERFACES OF DILUTE SODIUM OLEATE SOLUTIONS

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TABLE OF CONTENTS

INTRODUCTION

It is probable that no single class of compounds has been the subject of as much discussion in the chemical literature as have soaps. The countless investigations, and the manifold theories to account for their characteristics may be taken as a criterion of the importance of soaps in everyday life as well as an indication of the dissatisfaction with preëxisting theories which has been continually entertained.

The importance of soaps may be arbitrarily divided into two major units, namely, their theoretical significance, and their practical applications. Although by far the larger part of the study of soaps has been devoted to the utilitarian aspects of these compounds, a complete understanding of their behavior and properties would contribute much to the fuller comprehension of proteins, that enormous class of complex, biological substances to which the more simple soaps are analogous in their colloidal behavior.

Soaps are, in general, salts of a limited number of organic acids and the stronger inorganic bases. The organic acids used for soap-making are obtained by the hydrolysis of animal and vegetable fats. Combined with inorganic bases, these acids yield a class of compounds which stand intermediate between the inorganic and organic.

Further theoretical significance is attached to soaps because they offer a means of studying phenomena of the colloidal state of matter. In aqueous solutions, soaps possess the remarkable property of maintaining a suspension of finely divided oil droplets which would coalesce and separate if the soap were not present. The practical importance of these

compounds is almost entirely attributed to this ability to promote and maintain emulsions of water and oil. The functional properties of soaps in aqueous solution which enable them to prevent the coalescence of oil droplets are principally surface phenomena at the boundary between the oil droplets and the aqueous solution. The mechanism of the physical and chemical activity of soaps at the interfacial boundaries of their solutions constitutes the remaining theoretical aspect of these compounds.

The purpose of the investigation described in the following pages is, broadly, to study the interfacial phenomena exhibited by soap solutions under controlled conditions by a differential method. Although the mechanism of the activity of soaps at the interfacial boundary oil/soap solutions constituted the ultimate object of the work, surface phenomena at the interface vapor/soap solutions were not disregarded because these two types of boundaries are intimately related and, also, because both classes of interfaces derive their functions from the solutions themselves.

REVIEW OF THE LITERATURE

Soaps have been known and used as a commodity since ancient times. Pliny (52) wrote that soap was first made by the Gauls from goat suet and the ashes of the beech tree. It is only in comparatively recent times that any recorded work of importance has been done on these compounds.

Chevreul (9), in 1823, published a report of his researches on the fat from animal bodies. His report embodied a theory to account for the cleansing action of soap, which on the basis of his studies, he attributed to the ease with which fats could be emulsified in solutions of soap.

Berzelius (4), on the other hand, believed that the free alkali which resulted from the hydrolysis of the soap brought about the washing action by saponification of the grease which held the dirt, and thus permitted the dirt particles to escape.

Selmi (59), 1845, defined an emulsion as a system of two liquid phases one of which was dispersed in the other as globules.

Gad (20) and Brücke (6) and later Quincke (54), 1870-88, began the first systematic investigations of emulsions. They produced emulsions of oil-in-water by shaking together rancid oils and dilute solutions of alkalies. Quincke summed up the investigations in the surface tension theory of emulsification 1888, that the surface tension is lower between the oil and the alkali solution than it is between the oil and pure water.

The surface tension of soap solutions was studied by Gibbs (21), 1878, who showed that within very wide limits of concentration the

value is constant. Lord Rayleigh (56), 1890, proved that the surface tension of soap solutions changes with the freshness of the surface formed.

Hillyer (28), 1903, recognized the necessity of "a small surface tension between the oil and emulsifying agent".

Dennhardt (10), Krafft (33), and Spring (63), 1895-1910, investigated the properties of soaps in aqueous solutions. McBain and his students extended the work, and have exhaustively studied the nature and characteristics of soap in solution.

Since the beginning of the twentieth century new knowledge of the properties of matter, improved research methods and more sensitive instruments have led to rapid advances in the understanding of all natural phenomena. The investigations which have been carried out are much more thorough and accurate. In the field of soaps and emulsions the interpretations of experimental data have been increasingly complex and decreasingly contradictive. Therefore, in order to represent these investigations with the proper values and the greatest simplicity, they will be arranged chronologically under three distinct topics namely, (a) solutions of soap, (b) surface tension of soap solutions and (c) the interfacial boundary.

Kahlenberg and Schreiner (31), 1898, measured the electrical conductance of some soap solutions and concluded that soap solutions are not colloidal in nature because they contain conducting ions, and that soaps dissociate into acid soap and free alkali. Molecular weight determinations by the freezing point method were carried out on sodium oleate solutions. The apparent molecular weight of the solute was 512-560. These data indicate that sodium oleate dissolves as a double molecule.

Mayer, Schaeffer and Terrione (40), after an ultra-microscopic examination of solutions of the sodium salts of the fatty acids, pointed out that the higher members of the series, including soaps, were colloidally dispersed.

Commenting on salts of various metals and oleic acid, Von Weimarn (66), stated that the alkali oleates are soluble in water because the metal part of the salt is strongly active. The existence of free fatty acid ions is, therefore, improbable.

Shorter and Ellingworth (61) found that the addition of small quantities of alkali to solutions of the neutral salt increased the surface activity of the soaps. The effect was thought to be too large to result from the suppression of hydrolysis. It was suggested that the additional alkali may have caused an increase in the colloidal nature of the solution.

Beedle and Bolam (3) measured the alkalinity of sodium oleate solutions at 90°C. by determining the rate of catalysis of nitrosotriacetonamine. A maximum alkalinity was observed at concentration .05 normal.

McBain, Laing and Titley (45) determined the conductances of sodium oleate solutions between concentrations 0.6 normal and 0.01 normal.

Leeten (38) investigated the electrical conductivity of sodium oleate solutions over the interval of concentrations 0.2 normal to 0.001 normal and concluded that the hydrolysis constant of sodium oleate was very small.

McBain and Jenkins (44) were of the opinion that acid sodium oleate has approximately the composition Na_2H $oleate_3$ although its composition may vary with the concentration of the mother solution.

McBain and Buckingham (43) studied the hydrolysis of sodium palmitate solutions by extraction with para xylene. From the experimental data the conclusion is drawn that very little fatty acid is present in the solution

although appreciable hydrolysis takes place, and that the hydrolytic fatty acid is almost quantitatively converted into an acid soap. Thus the soap, in hydrolytic equilibrium, is an excellent buffer.

Summing up his investigations McBain (41) concluded that a true, complete, reversible equilibrium exists between the different colloidal and crystalloidal constituents. The unit is the colloidal aggregate, not the molecule or simple ion. The colloidal aggregate, a micelle, is large enough to be retained by the ultra filter. In dilute solutions the micelles dissociate into simple molecules. In another paper McBain (42) wrote: "The acid soap is in suspension either coarse or colloidal as the case may be, and it consists of something between the neutral soap, NaR, and the acid soap, $NaHR_2$, where R is the radical of fatty acid".

$$\text{Soap + Water} \rightleftharpoons \text{Acid Soap + Free Alkali}$$

"The distinctive behaviour of these (oleic acid) soaps is due to the fact that the formation of the hydrophilic ionic micelle persists into unusually low concentrations."

Since 1900 the surface tension of various soap solutions has been frequently investigated. The measurements of sodium oleate have been recorded more often and accurately.

Gibbs (22), 1906, gave a rigorous mathematical treatment to the phenomenon of interfacial adsorption and stated in mathematical form the relationship between surface energy and surface concentration. Gibbs final equation was reached almost entirely from theoretical considerations of the second law of thermodynamics. In its more common form the relationship is,

$$E = -\frac{c}{RT} \cdot \frac{d\sigma}{dc}$$ in which E = surface excess, σ = surface tension, c = concentration, R = gas constant, T = absolute temperature.

Stated in words the equation predicts that the excess of solute per unit volume of surface, as compared to a unit volume of the solution, is positive when the surface tension decreases with increasing concentration, and is negative when the surface tension increases with increasing concentration.

Milner (47) attempted to verify experimentally the Gibbs equation. Using the capillary rise method of determining surface tension, Milner obtained constant values for sodium oleate solutions of concentrations 0.002 normal and greater.

The study of liquid surfaces led to the proposal of the orientation theory of structure by Harkins (27) and Langmuir (35) independently. According to this theory the surface layers of molecules arrange themselves in such a way that the more active ends extend into the phase in which their activity is greater, the less active ends dip into the less active phase. The general law in the words of Harkins is that orientation at surfaces takes place "such as to make the transition to the adjacent phase less abrupt". Harkins and his collaborators stated also, that at concentration 0.002 normal, a solution of sodium oleate first presents a surface completely covered by a monomolecular layer. Concentrations of sodium oleate greater than 0.002 normal have saturated surfaces. These investigators used the drop weight method for surface tension determinations.

Walker (67) concluded after an investigation of the surface tension of solutions of several soaps that surface phenomena could be satisfactorily explained by McBain's theory if the additional assumption be made that surface tension lowering is limited not only by concentration in the surface layer, but also by the size of the colloidal particles.

Von Blumencron (65) noted that the lower the surface tension became, the easier foams were produced.

In a review of the more recent developments in the knowledge of soaps Zsigmondy and Thiessen (71) stated that the surface tension and foaming power stood in close relationship to the concentration of colloidal particles in the solution.

Lascaray (37) has presented a table of surface tension data for the sodium salts of fourteen of the fatty acids and confirmed the results of Dubrisay and Picard (13). These investigators show that surface properties change in regular fashion from the surface inactive sodium formate up to higher members of the series.

DuNoüy (14) employed the ring method for the determination of surface tension of various concentrations of sodium oleate.

The influence of various salts on the surface tension of sodium oleate solutions has been investigated stalagmometrically by Mikumo (46). The measurements show that of all ion effects those of H^+ and OH^- predominate. The addition of hydroxyl ions suppresses hydrolysis and thereby decreases the concentration of the acid soap. Under these conditions the surface tension rises to a maximum. The addition of hydrogen ions depresses the surface tension strongly because a large quantity of acid soap is formed. Although the addition of dilute alkali solution to the sodium oleate solutions increases the surface tension, the resulting soap solution is nevertheless more detergent, perhaps because the alkali exerts a peptizing action.

Johlin has examined the surface properties of aqueous solutions of sodium oleate both by the capillary rise method (29) and by the sessile bubble method (30). He criticized the capillary rise, drop weight, and ring methods, and was sustained by Washburn and Bigelow (69).

The data (30-a which Johlin submitted) indicate that equilibrium values of surface tension, obtained by the sessile bubble method, are considerably larger than the values reported by other investigators for the interval of concentration 0.002 normal and greater.

Since the earlier observation of Lord Rayleigh periodic changes in the surface tension of sodium oleate solutions have been recorded by DuNoüy (15), Kopaczewski and Szukiewicz (32), Johlin (29) (30) and Bulkley and Bitner (7). For the most part the observations have been that the surface tension decreases to a minimum and subsequently rises again to a constant value.

Ettisch and Koganei (16) have reported that the surface tension-concentration curve of sodium oleate shows no minimum although the sodium salts of glycocholic, cholic and taurochloric acids under the same conditions exhibit distinct fluctuations.

The study of the interface which exists between two immiscible phases has been concerned largely with the adsorption phenomena which occur at the interface. Donnan (11), 1899, first showed that emulsification was, in the case of the investigations of Gad, Brücke and Quincke, intimately related to the formation of a layer of soap at the oil-water interface. Gibbs' mathematical treatment of the thermodynamics of interfaces indicated the type of activity which made boundary phenomena so important.

Donnan and Potts (12) investigated the emulsifying powers of the various sodium salts of the fatty acids with respect to a pure hydrocarbon oil. Their observations showed that effective emulsifying powers are first exhibited by sodium laurate ($NaOOC\text{-}C_{11}H_{23}$). For each of the sodium salts of fatty acids above the laurate in the paraffin series

there was an optimum concentration for maximum emulsifying power. Donnan and Potts concluded that increased concentration took place at the oil-water boundary as Gibbs' rule predicted. These investigators concluded, in addition, that "changes in the interfacial tension at the boundary oil/water are connected with changes in electrical potential, in which the selective adsorption of ions probably plays a part", and also, that the emulsified oil droplets were enveloped by a "very viscous or possibly gelatinous film which offers resistance to the coalescence of the globules". Following Gibbs' rule this film is the result of adsorption which, in turn, is due to the effort on the part of the solution to offset the free interfacial energy.

Ramsden (55) verified the existence of films by an independent method which entailed the shaking of colloidal solutions with the result that fibrous or gelationous films of an irreversible character were formed as a consequence of adsorption.

Pickering (51) after an intensive study of soap emulsifiers concluded that the most significant factor in water and oil dispersions is the presence of finely divided particles, insoluble in the external phase, which coat the oil droplets and prevent their coalescence. In the case of sodium oleate the presence of "acid soap" as a finely divided solid was deemed supporting evidence.

Lewis (39) examined the system hydrocarbon oil-water-sodium glycocholate in order to show the quantitative significance of Gibbs' rule at the liquid/liquid interface. After determining the interfacial tension between the oil and various concentrations of sodium glycocholate by means of the drop pipette, Lewis emulsified a portion of the oil in a definite quantity of a glycocholate solution. Subsequent microscopic analysis was used to determine

the area of the oil drops, and the interfacial tension of the supernatant liquid was measured again. These data were substituted in Gibbs' equation and the degree of adsorption at the interface calculated. There was nearly eighty times as much adsorption observed experimentally as the equation predicted. Inasmuch as Gibbs' mathematical derivation was based on the assumption that the solute and solvent form a single phase, and that adsorption of the solute would not change the entropy of the molecules in the surface layer, Lewis concluded that the observed discrepancy is due to the fact that colloidal substances form a gelatinous or semi-solid film around the oil droplets.

Freundlich (19) proposed the adsorption isotherm, a quite empirical relationship, which equates an exponential function of the equilibrium concentration of the solute and the ratio of the mass of solute adsorbed to the mass of adsorbing material.

The general theory of surfaces in emulsoid systems was outlined by Bancroft (1) who postulated that the film separating the oil and water constitutes a third phase which is wetted on one side by the water and on the other side by the oil. Because the surface tension of water is different from that of the oil, there exists a difference of surface tension between the two sides of the film when the latter constitutes an oil/water interface. The film under these conditions tends to envelop the liquid on the side of the higher surface tension.

Briggs (5) emulsified benzene in sodium oleate solutions of differing concentrations, allowed the emulsions to cream, and removed an aliquot of the aqueous layer. A portion of the stock solution and the aliquot from the aqueous layer were titrated with hydrochloric acid. He took the decrease of alkali content due to emulsification as a measure of the sodium oleate adsorbed. The data were calculated by employing Freundlich's equation and

the conclusion was reached that the sodium oleate adsorbed agrees qualitatively with the mass required by the adsorption theorem except for dilute solutions in which the predicted quantity exceeds the observed.

In order to determine the "surface activity" of acid soap, which is the result of hydrolysis, Shorter (60) investigated the effect of various proportions of hydrochloric acid in the soap solutions. Changes of detergency were recorded in the drop numbers which the acidified soap solutions exhibited when pure benzene was used in the stalagmometer. The chemical effect of acidifying the solution more and more strongly is the conversion of increasingly larger quantities of the neutral to the insoluble "acid soap". Shorter's data showed that as the concentration of hydrochloric acid in the soap solution was increased, the interfacial tension became higher and higher until a value practically equal to that for pure water was attained. The interpretation of these data was an affirmation of the previously held assumption that "acid soap" is not surface active, and also, that alkalies in excess increase the surface activity of soaps.

Nugent (49) has found by an arbitrary method that the rate of adsorption of gelatin on benzene droplets is essentially a parabolic relationship between the quantity adsorbed in the time stated.

The torsion pendulum balance was employed by Wilson and Fries (70) in the measurement of the superficial viscosity of films. In the case of sodium oleate these investigators found marked adsorption at the vapor/solution intefface but only in concentrations of 1/5000 or greater is there any evidence of a plastic solid film.

Griffin (23) prepared emulsions of kerosene in sodium oleate and analyzed the cream for fatty acid. His calculations of the area occupied by one molecule agree with those given by Langmuir (36). Griffin concluded

from his work that unless there is sufficient soap to form a unimolecular film the emulsion will be unstable.

Rieman and van der Meulen (58) found monomolecular films of sodium oleate adsorbed around the oil droplets in their emulsions, and concluded that the adsorbed soap is in dynamic equilibrium with that dissolved in the aqueous phase.

The changes in properties of solutions of sodium oleate due to the addition of benzene and oleic acid were investigated by Hahne (24). Inasmuch as the excesses of oleic acid caused the conductance to decrease, Hahne thought that the micelles increase in size. He concluded, also, that the presence of benzene exerts an influence upon either the composition or the mobility of the micelles or upon both simultaneously. He confirmed the conclusion of other investigators (38) (65) that free oleic acid serves as the nucleus for the formation of colloidal micelles.

Some of Gibbs' work (22) has been expanded and criticized by Bancroft and Tucker (2), who showed that the general theory outlined by Bancroft (1) was implicitly formulated by Gibbs' and that the existence of a film possessing different surface tensions on either side is not incompatible with the idea of an oriented monomolecular envelope.

Fall (17) found that sodium oleate solutions between 0.156% and 0.625% concentration exhibit the maximum detergent action.

Vincent (64) observed that manganese dioxide colloidally dispersed in a soap solution had acquired a negative charge which he attributed to the adsorption on the MnO_2 particle of negative oleate, palmitate, or other true ions of the fatty acids. As the concentration of the solution increases adsorption of the positive ion increases. Eventually a concentration is reached at which positive and negative ions are adsorbed at the same rate. Under these conditions the MnO_2 particle possesses no charge and an unstable suspension results.

Harkins (26) summed up the investigations which he and his collaborators have made in regard to surface tension and adsorption. He believed that adsorption at surfaces resulted largely in a unimolecular layer. The electrical effects of an interfacial potential difference, which McBain and his associates suggested as the cause of the failure of the Gibbs' theorem, were considered insufficient by Harkins. He pointed out that the thermodynamic potentials and other thermodynamic magnitudes exist at the surface with whatever potential difference the surface may have.

Laing, McBain, and Harrison (34) studied the removal of sodium oleate from solution in the films of bubbles. Nitrogen was permitted to bubble slowly through the solution. The bubbles, consisting of nitrogen gas surrounded by a film of the soap, were collected and analyzed. The analysis showed that the soap in the film contained an excess of oleic acid approximately, 3 sodium oleate/2H oleate. Their calculations showed nearly twice as much solute as could be packed into a monomolecular film. They concluded that the adsorbed soap is in hydrolytic equilibrium with that dissolved, but its hydrolysis is completely suppressed by a small quantity of alkali.

Nonaka (48) concluded after a study of cataphoresis in soap solutions that the surface active material is the ionic fatty micelle. In another paper (48a) Nonaka reported adsorption experiments in which the interfaces between benzene and toluene and sodium oleate solutions were examined with the Donnan pipette. He was led to believe that the quantity of adsorbed soap was larger than could be packed into a unimolecular layer and is, therefore, in a monomicellar layer.

Rhodes and Bascom (57) investigated the influence of hydrogen ion concentration on the detergency of soap solutions. Although the data recorded by these authors agreed qualitatively with those reported by

Vincent, they held the latter's hypothesis of specific ion adsorption to be untenable because they found maximum detergent effects not at equal alkali ion concentrations, but rather, at the same alkalinity with highly different concentrations of basic ions. In comparison with buffer salts such as sodium carbonate and trisodium phosphate, the efficiency of sodium hydroxide in increasing detergent action is comparatively low.

Fischer and Harkins (18) published evidence which indicates that sodium oleate is adsorbed in emulsions of oil-in-water as a unimolecular layer around the oil droplets.

DISCUSSION

The general theory of the nature of the interface between any colloidal particle and its surrounding medium has been enhanced by the comparatively recent work of Gouy, Pauli and Engel, McBain, Debye and Huckel, Bjerrum and others. Pennicuick (50) has reviewed and extended the work. These investigators have visualized the colloidal particle as a huge multi-valent ion which owes its electrical charge to the dissociation of surface molecules. Contra ions, those true electrical integrals which migrate a short distance into the dispersion medium and leave their counterparts imbedded in the surface of the colloidal unit, are governed in their activity by the laws of molecular feactions. This concept is particularly satisfactory because it explains the origin of the electrical charge in terms of phenomena which have been amply and completely proved - ionization.

Although investigators have failed in most cases to verify experimentally the quantitative aspects of Gibbs' adsorption equation, the thermodynamic treatment of the interface by Gibbs is none the less significant. The energy relationships are always true but the predicted magnitude of energy changes may quite frequently be invalidated by the formation of a third phase, the film, or by the presence of colloidal solutes, association, and such disturbing conditions. Gibbs' rule was developed entirely from a consideration of the free energy at the surfaces of a single homogeneous phase. For this reason quantitative experimental verification in a system which is colloidal and which probably presents a highly viscous second phase at its interfaces can not be expected until proper allowances are made for vitiating influences.

The orientation theory of surface structure proposed by Harkins and Langmuir has been shown by Bancroft and Tucker (2) to be a corollary of

Gibbs more general rule. If two liquids in contact do not form a single phase, free energy must be present at the liquid/liquid boundary in sufficient quantity to offset the tendency of the liquids to mix. Gibbs' postulated a unidirectional flow of solute to the interface such that the free energy should be equalized. The orientation theory is more specific because it requires the solute at the interface to arrange itself in a way that shall make the free energy of transition between the two phases least abrupt.

The dual surface tension theory of Bancroft is another corollary of Gibbs' rule. In order to reconcile the formation of the interfacial film with Gibbs' considerations of two homogeneous phases, Bancroft treated of the film as a third phase which would be formed according to the second law of thermodynamics. The existence of a third phase between the original two demands the consideration of two free energy regions, the contact surfaces between each original phase and the film. The dual surface tension theory is, therefore, not incompatible with the orientation theory but rather simply fuses an oriented layer into a continuous, more homogeneous third phase.

Milner failed to verify Gibbs' equation experimentally for the vapor/solution interface of sodium oleate, but later investigators have shown that this soap dissolves as a colloidal dispersion. The work of Johlin and Laing, McBain, and Harrison has emphasized the fact that surface concentration phenomena predicted by Gibbs' equation are wrong not only in magnitude but also in sign for all but extremely dilute solutions. The deviation in magnitude may be explained quite readily by the nature of the solution, but the error in sign indicates a fundamental misconception.

At the interface oil/sodium glycocholate solution Lewis found eighty times as much adsorption experimentally as Gibbs' rule predicted. The

discrepancy has been attributed to the colloidal nature of the solution and to the formation of the film.

Vincent's hypothesis of specific ion adsorption to account for the electrical charge is untenable until the functions and relative positions of the oppositely charged concomitants of the specific ions are defined. Specific ion adsorption is either a restatement of the multi-valent ion theory of surface structure in which the oppositely charged ions are neglected or else it rejects the classical magnetic attraction of opposite charges. Rhodes and Bascom have published data which indicate that Vincent's hypothesis is inadequate. The adsorption effects to be expected from the specific ion hypothesis were found by Rhodes and Bascom not at equivalent concentrations of the alkali metal ions as predicted, but rather at equivalent hydroxyl ion concentrations. This observation introduces the possibility of hydrolytic effects to explain Vincent's results.

Shorter's investigations, as well as all other studies, in which the drop pipette has been employed, are subject to criticism. Drops from the tip of the Donnan pipette do not measure the equilibrium condition between the oil and the solution because they are formed and released in a time interval too short to permit diffusion. Shorter's data can be taken then only as an indication of the amount of solute in a freshly formed oil/solution interface and not as a measure of interfacial free energy at equilibrium. Lewis used the same method and substituted his nearly instantaneous data in Gibbs equilibrium equation.

In order to verify Freundlich's adsorption equation Briggs titrated the sodium oleate solution with hydrochloric acid both before and after emulsification, and calculated the quantity of soap adsorbed from the difference. The assumption in this procedure, that one atom of sodium is lost from the aqueous solution for each molecule of sodium oleate adsorbed, has been criticized by Clayton (8) who suggested that the possibility of

hydrolysis had been neglected. Titration methods have been criticized also by McBain. The latter pointed out that titration of one component of an equilibrium system will not give a true estimation of the original equilibrium which will progressively shift by mass action as the titration procedure removes more and more of the component in question.

Hahne concluded from his conductivity measurements of sodium oleate and benzene intimately mixed that benzene exerts an influence upon the kind or arrangement of the ionic micelles of sodium oleate. Decreases of conductance of the original solutions, which took place when excesses of oleic acid were introduced, were believed by Hahne to be caused by the lessened mobility of the conducting particles. If hydrolysis of the sodium oleate produced any highly conducting free sodium hydroxide, neutralization by oleic acid would cause the conductance to fall in the same way. Hahne gave no data relative to the area of the benzene droplets hence no conclusions may be reached anent adsorption.

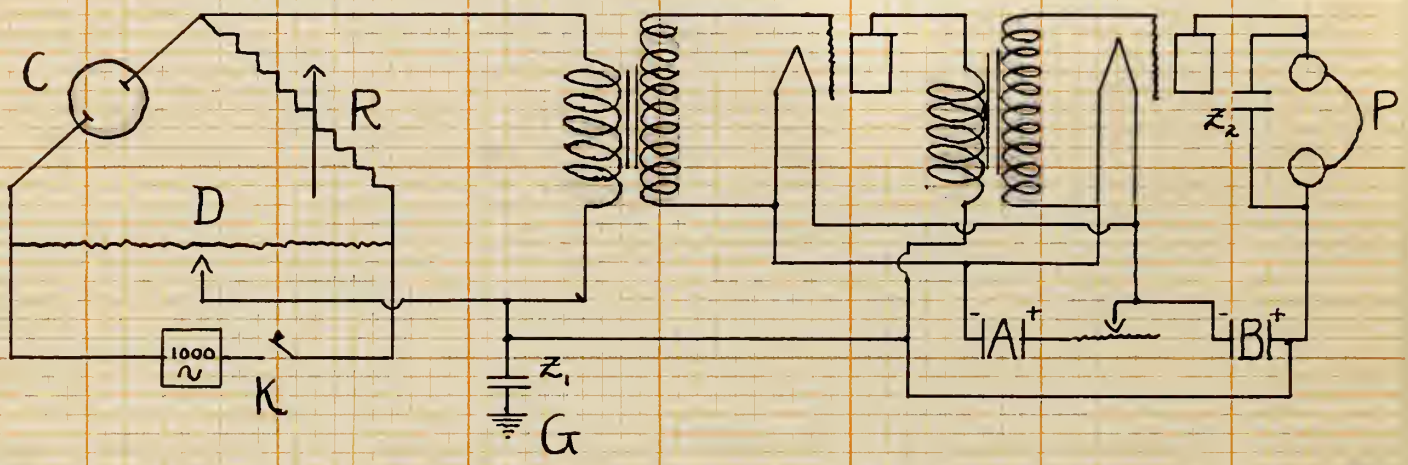
Smyth (62) and his collaborators have conceived molecules as dipoles or tiny magnets which derive their electrical properties from the configuration of the structure. The relative positions, the magnitudes, the distances apart, and the proximity to the external molecular shell of the residual atomic charges of opposite sign, determine the properties of the molecules. Water molecules in this light are small compact highly polarized units with their charges near the external surface. They attract each other strongly and exhibit association effects not observed in most other liquids. Organic molecules, on the other hand, are comparatively large and possess scattered dipoles whose positions in the molecular structure effectively reduce the magnetic attractions for surrounding molecules. Water and organic liquids do not mix intimately because the magnetic forces exerted by water molecules on each other are greater than the forces which act between the water

molecules and the effectively non-magnetic organic molecules.

When two immiscible liquids are in contact, the thermodynamic conception requires free interfacial energy in sufficient quantity to prevent mixing. Each of the liquid phases constitutes a system whose free energy is vastly different from that of the other system. These systems impinge at a liquid/liquid boundary at which an abrupt change in energy content marks the transition from one system to the other. The difference in magnitude between the two free energy systems is the free interfacial energy. Because free energy can be only a manifestation of the more fundamental electrical nature of things, the high free energy content of aqueous systems must arise from the magnetic properties of the water molecules, and the low free energy content of organic oils must due to the absence of magnetism from the organic structure. The thermodynamic flow will be from the system of greater energy toward that of lesser, or specifically, from the aqueous phase toward its boundaries.

Oleic acid is insoluble in water, but extremely soluble in oils and must, therefore, be a non polar liquid. The sodium salt of oleic acid, sodium oleate, is soluble in water but insoluble in oils, a consequence of the polarizing influence of sodium. Acid sodium oleate, the intermediate compound of sodium oleate and oleic acid (3 Na oleate. 2 oleic acid), should be less soluble than sodium oleate itself, and consequently exhibit a greater tendency to be adsorbed at the interfaces of a solution which contains these two constituents. In other words the more soluble constituents should possess the least tendency to leave the aqueous solution - the lesser fugacity.

FIGURE 1



THE CONDUCTIVITY BRIDGE CIRCUIT

PURPOSE AND METHOD

The purpose of this investigation has been a study of the interfacial boundaries of oil/sodium oleate solutions in order to define the mechanism of interfacial adsorption as a function of the sodium oleate solution. The range of concentrations involved is that for which Gibbs' rule predicts negative adsorption.

The method employed has been that of electrical conductivity. By layering an oil on a sodium oleate solution in a conductivity cell, changes in resistance may be observed without undesirable effects on the equilibrium. Furthermore, sufficient time intervals may be used in order that static conditions may be more nearly realized. In addition the conductivity measurements may be interpreted in the light of molecular equilibria whereas surface phenomena alone may not.

APPARATUS AND MATERIALS

A Wheatstone bridge (Fig. 1) was used for the conductivity measurements. The entire bridge circuit consisted of a Kohlrausch bridge, manufactured by Leeds and Northrup, an hundred thousand ohm precision resistance box made by the same company, an Atwater-Kent two stage audio frequency amplifier and headphones to detect the minimum. A General Radio microphone hummer supplied the thousand cycle/second oscillating current. A similar apparatus has been described in the literature by Hall and Adams (25).

The bridge was set up so that the cell could be placed in the thermostat. The ground connections indicated in the diagram remove undesirable noises. Heavy, low resistance copper wire was used for wiring. With the audio amplifier the apparatus gave a very sharp, clear minimum.

The conductivity cell was the Freas type. Connections from the cell to the bridge were made by means of mercury wells. The electrodes of the cell were coated with platinum black after the method outlined by Popoff (53). The cell constant was about 0.3595 (subject to calibration curve).

The entire bridge assembly was calibrated according to the method suggested by Wark (68). Irregularities in the bridge wire are thrown into a varying cell constant which may be obtained for any particular bridge reading, with corrections included, by reference to a calibration curve.

Conductivity water was made by two distillations of the laboratory distilled water. The water was first distilled from alkaline potassium dichromate solution and the product, after treatment with Nessler's reagent to remove ammonia, was distilled and collected for use. The water obtained in this way had a specific conductance of about $.9 \times 10^{-6}$ mhos.

The sodium oleate, which was used to make the various concentrations, was obtained by twice recrystallizing Kahlbaum's "Purest" sodium oleate from methyl alcohol. The product was dried *in vacuo* at room temperature.

The benzene and toluene were Eastman Kodak's first quality. The meta-xylene, hexane and heptane were technical grade from the same company. The motor oil and Russian mineral oil were commercial products.

EXPERIMENTAL

The first part of the entire investigation was concerned with the determination of equivalent conductances of sodium oleate solutions between the limiting concentrations 0.12 normal and 0.0001 normal. These measurements were made to determine the effect of dilution upon the hydrolytic system which characterizes sodium oleate in aqueous solution. Comparison of surface tension values with the conductivity data have been made in order to define the mechanism of the activity of sodium oleate at the vapor/solution interface.

A stock solution of sodium oleate in conductivity water was produced by placing a weighed quantity of pure sodium oleate in a standard volumetric flask and adding the necessary water. This solution was then transferred to a Pyrex bottle which was fitted with ground glass stopper. The glass stopper was sealed in with paraffin to exclude contamination from the air.

The stock solution was allowed to stand for several days until equilibrium could be attained. Two aliquots of the solution were then transferred to the clean, dry conductivity cell by means of a calibrated pipette. The cell was placed in the thermostat at 25°C. In order to insure surface and thermal equilibrium in the solution determinations of conductance were made after the solution had remained in the bath for thirty minutes.

In the meantime the conductance of the freshly distilled water, which was to be used for dilution, was determined and checked in another cell after it had had sufficient time to reach the temperature of the bath.

After the initial reading of the sodium oleate solution had been recorded and verified, one aliquot of the solution was removed by means of a calibrated receiving pipette and an aliquot of the conductivity water added to replace it. The result of this operation was to exactly halve the

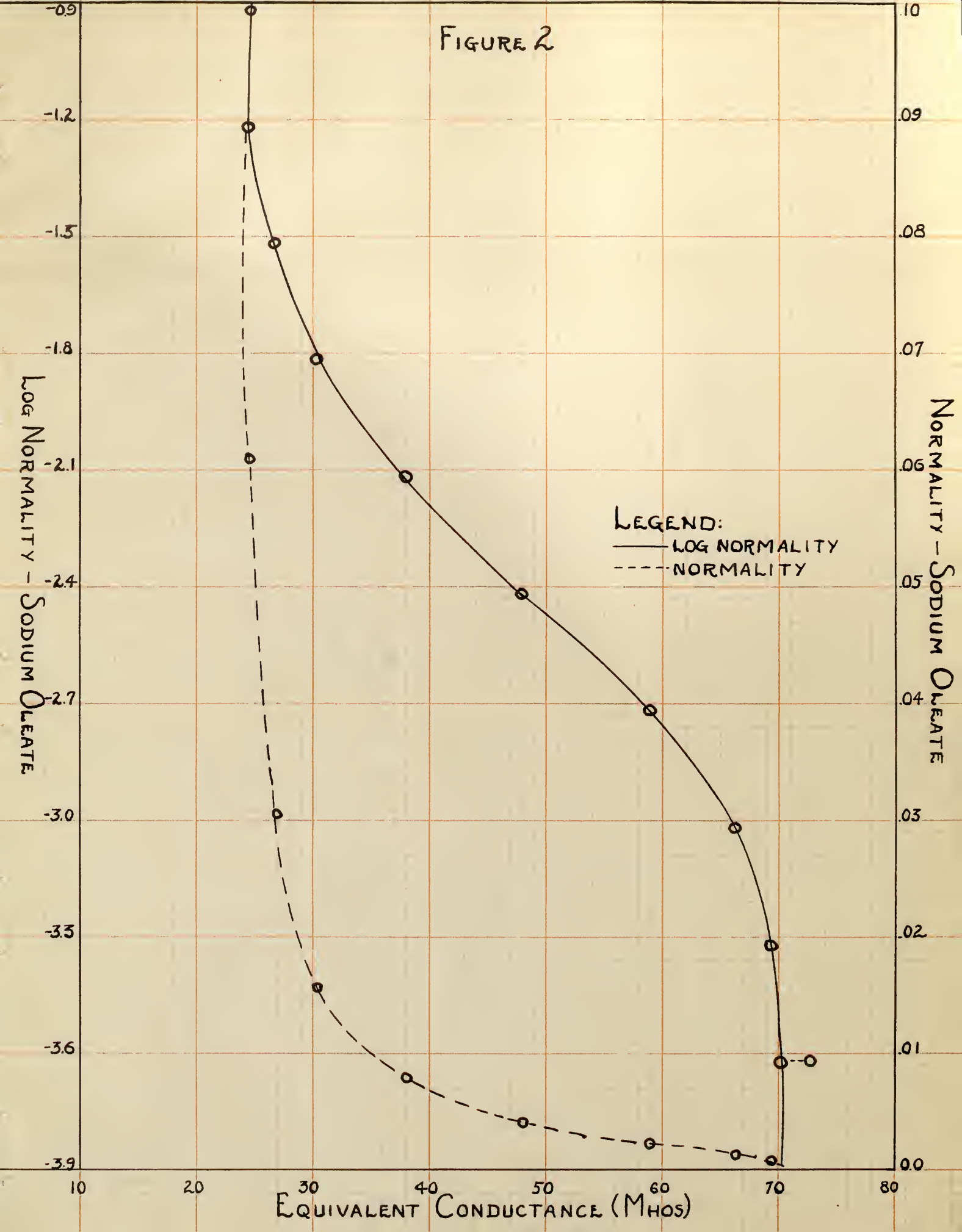


FIGURE 2
-0.9
-1.2
-1.5
-1.8
-2.1
-2.4
-2.7
-3.0
-3.3
-3.6
-3.9
LOG NORMALITY - SODIUM OLEATE
.10
.09
.08
.07
.06
.05
.04
.03
.02
.01
0.0
NORMALITY - SODIUM OLEATE
LEGEND:
LOG NORMALITY
NORMALITY
10
20
30
40
50
60
70
80
EQUIVALENT CONDUCTANCE (MHOS)

concentration of sodium oleate in the cell. After thirty minutes the measurements were recorded again and the operation repeated.

The solutions were mixed carefully in order to avoid foaming and suspended air bubbles. The deleterious action of atmospheric carbon dioxide was recognized and avoided as much as possible.

A typical set of data obtained in this way is presented in Table I. These data have been plotted (Fig. 2) in order to show more clearly the relationship of conductance to dilution. Johlin's surface tension data have been plotted also for comparison (Fig. 4).

Table I

The Equivalent Conductance of Sodium Oleate Solution at Different Concentrations (Temp. 25°C.)

Concentration (Normality)	Log Concentration	Equivalent Conductance
H_2O		0.83×10^{-6}
0.1216	-0.9150	24.75
0.0608	-1.2161	24.46
0.0304	-1.5171	26.87
0.0152	-1.8181	31.05
0.0076	-2.1190	37.88
0.0038	-2.4200	47.79
0.0019	-2.7210	58.68
0.0095	-3.0220	66.00
0.00048	-3.3290	69.03
0.00024	-3.6300	69.90
0.00024 (13 hrs.later)	-3.6300	72.42

The conductance-log normality curve of sodium oleate (Fig. 2) is characterized by a decided change in trend at concentration 0.002 normal. Although the surface tension-concentration curve (Fig. 4) changes in trend at the same concentration spurious effects due to dissolved carbon dioxide have not been entirely eliminated because it is extremely difficult to obtain pure water which contains no dissolved carbon dioxide.

When the sodium oleate solution is diluted, the solute undergoes hydrolysis and, as a consequence, sets free some sodium hydroxide. In aqueous solution pure sodium hydroxide approaches 243 mhos as the limiting value of equivalent conductance. Sodium carbonate, on the other hand, approaches 103 mhos as a limit. It is conceivable then that the formation of sodium carbonate by the interaction of free sodium hydroxide and dissolved carbon dioxide could effect the curvature very decidedly as dilution increased the concentration of carbonic acid.

In order to compensate for such an effect the following procedure was followed. The conductances of sodium oleate and sodium hydroxide were determined simultaneously in order that the same water could be used for the dilution of each. It was then assumed that the sodium hydroxide solution recorded the carbonic acid effect in the sodium oleate solution. Subtraction of the specific conductance of the sodium hydroxide solution from that of the sodium oleate solution should leave only <u>real</u> dilution or hydrolytic phenomena. This procedure is not greatly unlike that ordinarily used for "water correction".

The date obtained by the process just outlined are given in Table II. The same data have been plotted (Fig. 3) so that any irregularities would be emphasized.

FIGURE 3

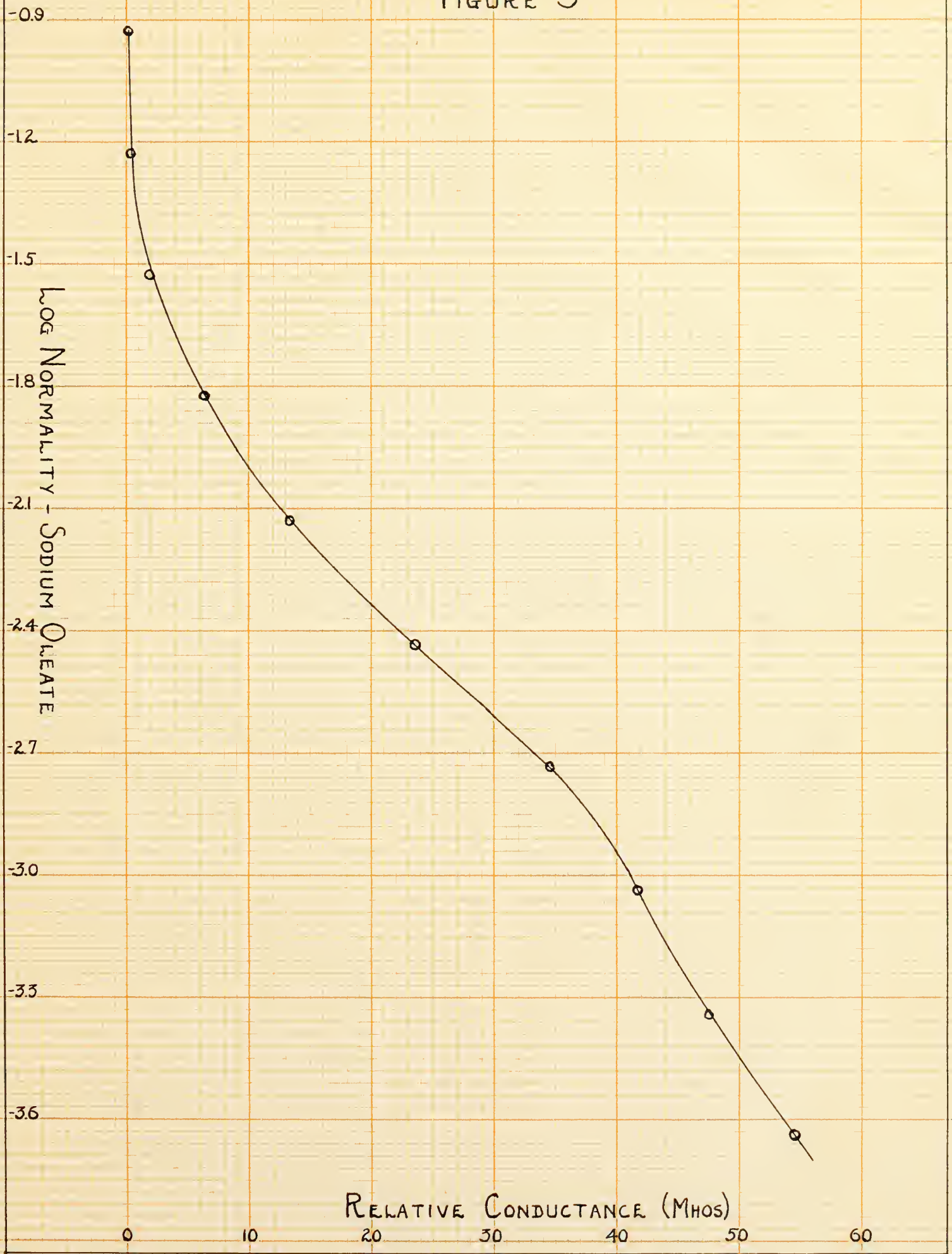

-0.9
-1.2
-1.5
-1.8
-2.1
-2.4
-2.7
-3.0
-3.3
-3.6
LOG NORMALITY - SODIUM OLEATE
0
10
20
30
40
50
60
RELATIVE CONDUCTANCE (MHOS)

FIGURE 4

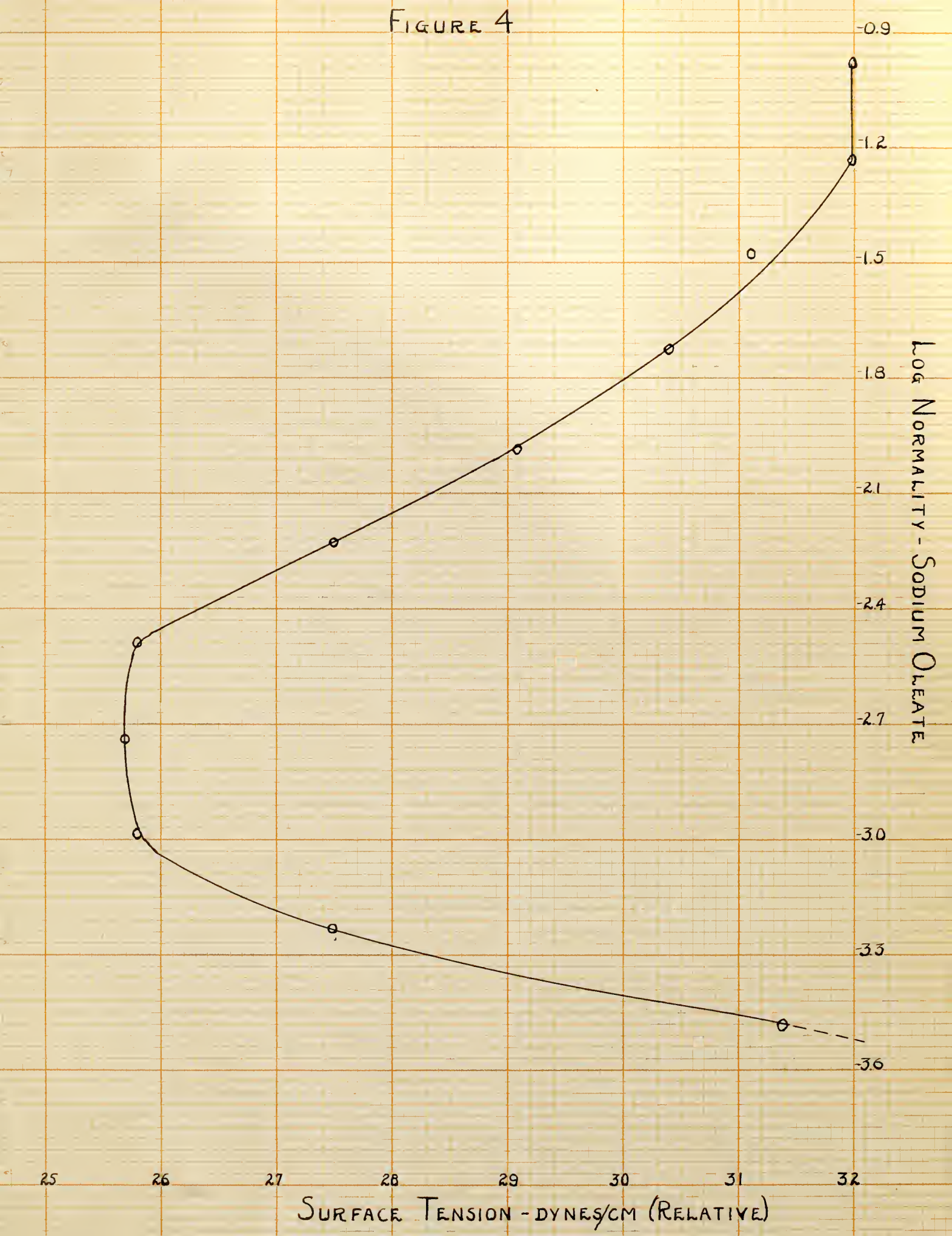

-0.9
-1.2
-1.5
-1.8
-2.1
-2.4
-2.7
-3.0
-3.3
-3.6
LOG NORMALITY - SODIUM OLEATE
25
26
27
28
29
30
31
32
SURFACE TENSION - DYNES/CM (RELATIVE)

Table II

Equivalent Conductance of Sodium Oleate at 25°C.

Corrected for Dissolved Carbon Dioxide.

Normality	Log Normality	Equivalent Conductance Corrected
.118	-.9281	0
.059	-1.229	.339
.0295	-1.530	1.976
.01475	-1.831	6.353
.0074	-2.132	13.33
.0037	-2.433	23.65
.0018	-2.734	34.50
.00092	-3.035	41.45
.00046	-3.336	47.40
.00023	-3.637	54.32

Table III

(See Figure 4)

The Variation of Surface Tension with Concentration

(Data of J. M. Johlin (30-a))

Normality	Log Normality	Relative Surface Tension in Dynes per cm.
.164	-.7852	32.0
.1038	-.9830	32.0
.0585	-1.233	32.0
.0329	-1.483	31.1
.0185	-1.733	30.4
.0104	-1.983	29.1
.0059	-2.233	27.5
.0033	-2.483	25.8
.0019	-2.733	25.7
.0010	-2.983	25.8
.0006	-3.233	27.5
.0003	-3.482	31.4
.0002	-3.733	35.4
.0001	-3.983	37.6

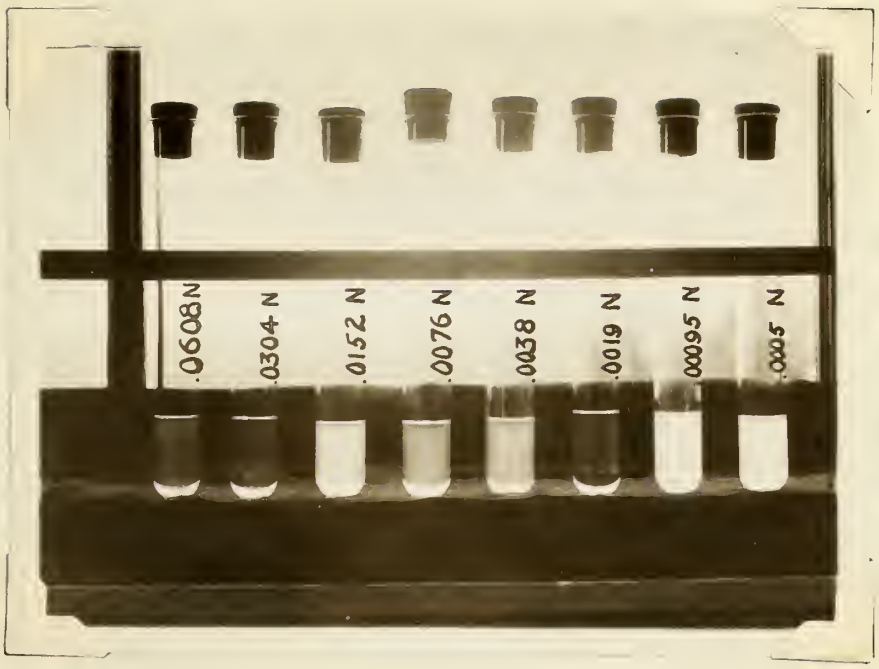
The graph of these data (Fig. 3) shows clearly that the "break" in the curve at 0.002 normal is not to be attributed to the effect of carbon dioxide. It is, therefore, due to a change in some peoperty of the solution. Furthermore, although the carbonic acid correction eliminates the possibility of contamination, and clarifies the nature of the "break", the original uncorrected curve (Fig. 2) is more significant because some dissolved carbon dioxide is inherent in the solution regardless of the particular experiment involved.

The corrected curve may be regarded as the absolute increases of conductance with dilution. As the dilution is increased, hydrolysis results in the formation of more and more of the highly conducting base, sodium hydroxide. If the increases in the mobility of the colloidal miscelles with dilution be neglected, the corrected curve is largely a representation of increasing hydrolysis as it is measured by conductance.

In addition to sodium hydroxide, difficultly soluble acid sodium oleate is formed by hydrolysis. The characteristic appearance of acid sodium oleate is a finely divided solid in colloidal suspension has been recorded in a photograph (Fig. 5). The turbidity disappears when a small quantity of dilute alkali is added to the solution. The effect of the alkali is the suppression of hydrolysis and the formation of the more soluble sodium oleate.

The photograph shows that a 0.002 normal solution of sodium oleate is clear. It was observed that the intense turbidity of solutions less than 0.002 normal developed in a relatively short time. The fainter turbidity in concentrations greater than 0.002 normal developed slowly. The more concentrated solutions which appear transparent in the photograph have in reality a finely crystalline precipitate deposited in the tubes. The abrupt change in the quantity of suspended acid sodium oleate at 0.002 normal indicates a change within the solution itself.

FIGURE 5



Solutions of concentration 0.002 normal or greater froth readily. The foam is very stable. Solutions of concentration less than 0.002 normal, on the other hand, do not promote stable foams. The clarification of these solutions with alkali does not appreciably change their frothing powers.

The quantity of suspended acid sodium oleate, the amount of free sodium hydroxide as measured by conductance and the foaming tendency of these solutions all undergo an abrupt change at 0.002 normal. The same concentration is characterized by the minimum surface tension (Fig. 4) which can be obtained with neutral sodium oleate in water.

Gibbs' equation for surface concentration $E = -\frac{c}{RT}\frac{d\sigma}{dc}$ requires that the slope of the surface tension concentration relationship $\frac{d\sigma}{dc}$ be negative in order that E, the surface excess, shall be positive. At 0.002 normal (Fig. 4) the slope of the surface tension-concentration curve becomes zero and makes E zero. Then as the concentration increases the slope becomes positive and E becomes negative. Gibbs' rule is commonly supposed to fail in those concentrations for which E is "in error both in magnitude and sign".

It has been shown (Figs. 2, 3, 4, & 5) that an abrupt change in the properties of sodium oleate solutions takes place at the concentration for which E is zero and that at least one new characteristic, foaming, is exhibited by solutions for which E is negative. Gibbs' equation cannot be applied directly, however, because the solution is colloidal.

Harkins has concluded that the surfaces of sodium oleate solutions are completely saturated at concentration 0.002 normal or greater. Obviously no further concentration can be expected although the character of the adsorbed material could change in such a way as to allow the surface tension to increase, but at the same time to maintain a saturated surface.

Table IV

(See Fig. 6)

The Relationship of Surface Tension to Conductance of Sodium Oleate at 25°C.

Normality	Surface Tension (Rel.) in Dynes per cm.	Relative Conductance in Mhos
.118	32.0	0
.059	32.0	.34
.0295	31.1	1.98
.0148	29.4	6.35
.0074	28.2	13.33
.0037	26.1	23.65
.00185	25.7	34.50
.00092	25.9	41.45
.00046	26.1	47.40

The regularity of the relationship (Fig. 6) between surface tension (from Fig. 4) and increases of conductance (from Fig. 3) for the various concentrations greater than 0.002 normal indicates that as conductance decreases, surface tension increases. Since, moreover, decreasing conductance is due almost entirely to decreasing hydrolysis, the increase of surface tension with concentration must be related to the formation of sodium oleate from acid sodium oleate as hydrolysis is suppressed.

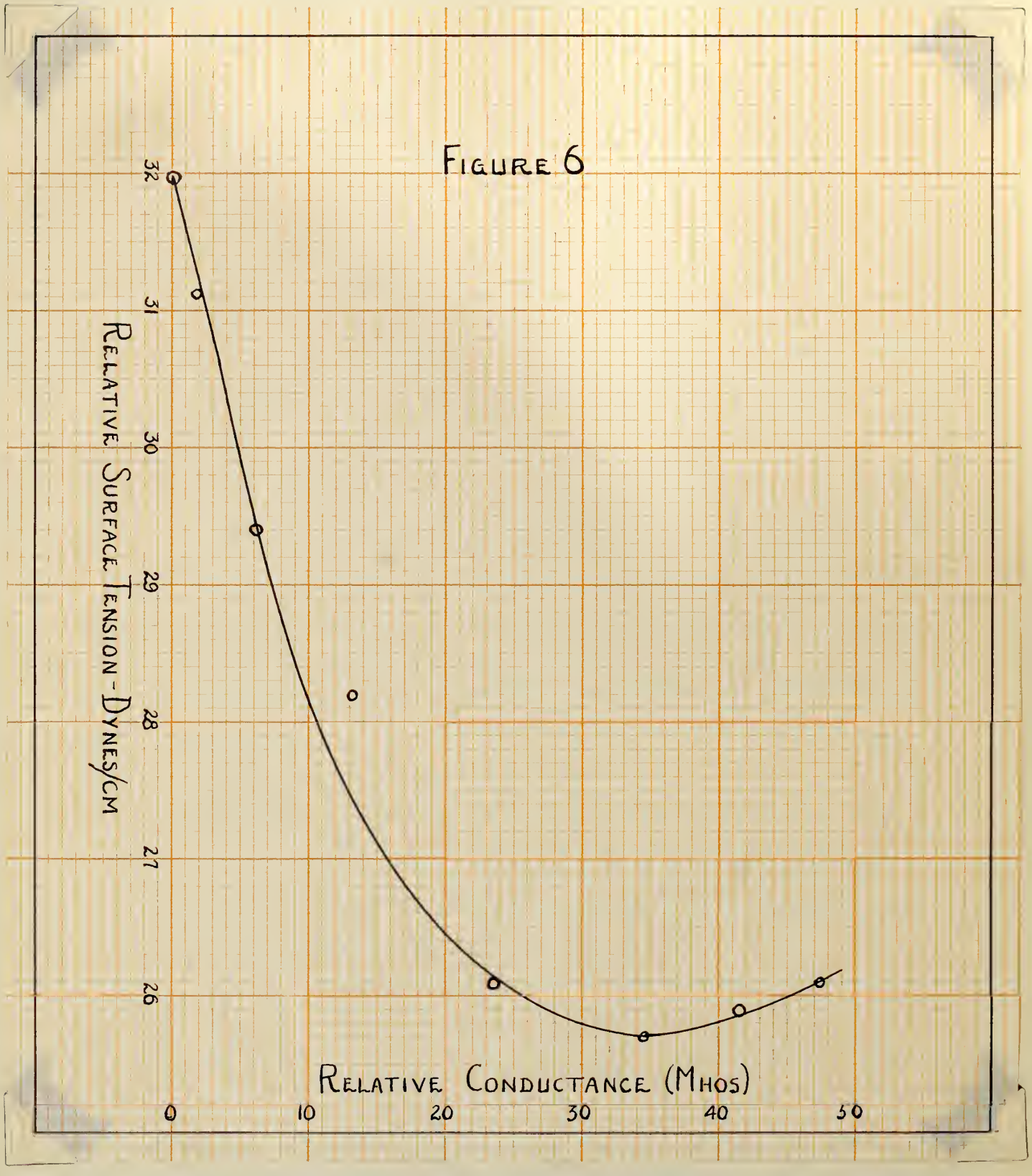


FIGURE 6
RELATIVE SURFACE TENSION - DYNES/CM
32
31
30
29
28
27
26
RELATIVE CONDUCTANCE (MHOS)
0
10
20
30
40
50

Adsorption at the Interface Oil/Sodium Oleate Solution

In practice, the most important interface of a soap solution is that at which it impinges on an oil or solid. At the oil/solution boundary adsorption takes place to the extent that the oil may become colloidally dispersed as droplets in the solution. In this second part of the investigation the interface has been studied under carefully controlled conditions in order that both surface tension and interfacial tension could be more accurately qualified.

The method employed in the study of interfacial adsorption at the oil/solution boundary was essentially the same as that used for the conductivity measurements. An accurately measured ten cubic centimeter aliquot of the sodium oleate solution was placed in the conductivity cell and allowed to reach surface and thermal equilibrium in the thermostat at 25°C. The conductance of the solution was then measured. A two cubic centimeter portion of the oil was then carefully layered on the surface of the solution in the cell and the time noted. Readings of time and conductance were sporadically recorded as indications of the progress of adsorption.

The interface was investigated under conditions such that each of the possible variables in turn was allowed to change while the others were held constant. In the first case investigated the oil, benzene, and the interfacial area were held constant and different concentrations of the sodium oleate solution were used. The increments of conductance due to adsorption at the benzene/sodium oleate solution interface for 23 hours have been calculated and tabulated in Table V.

Figure 7

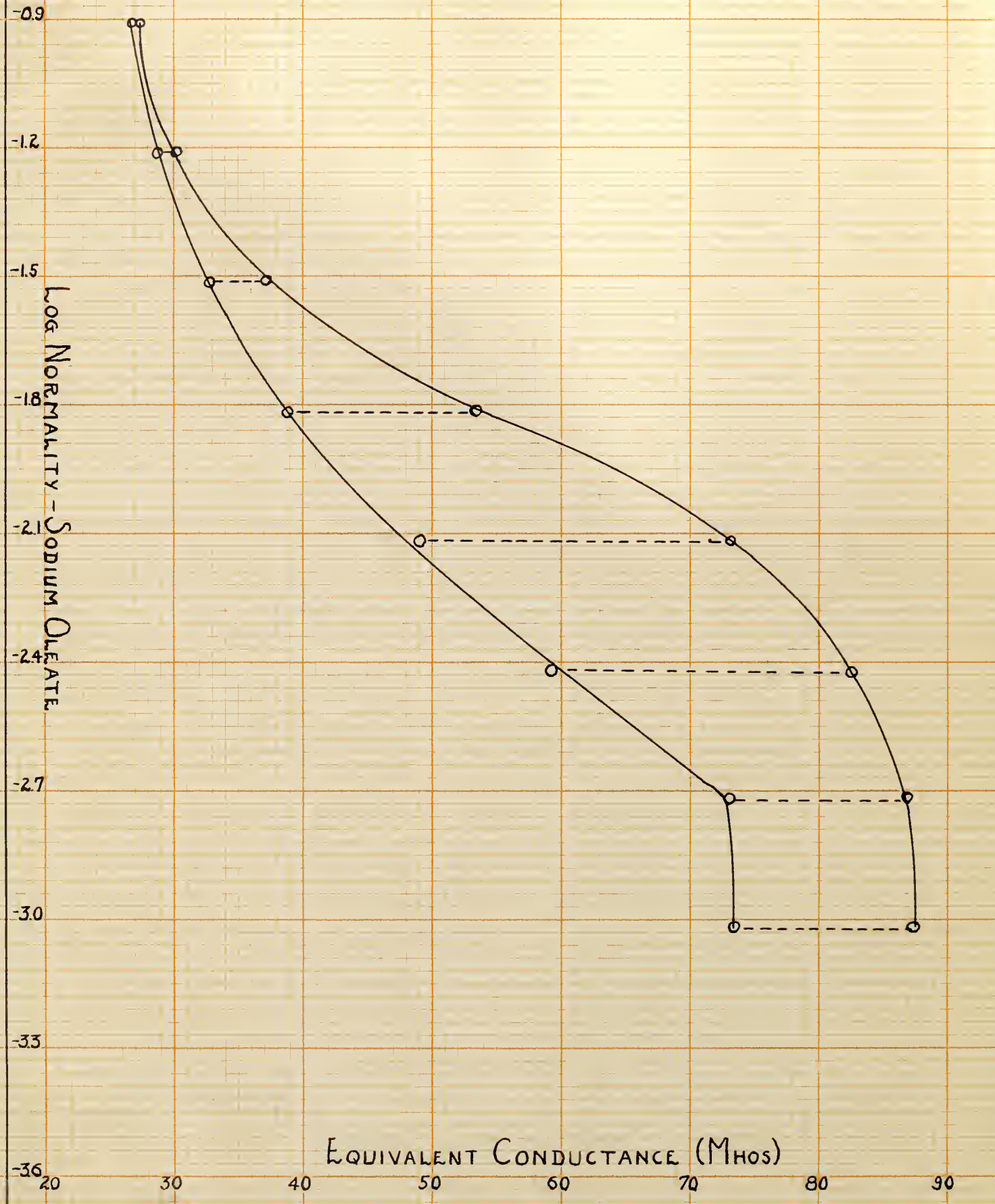

-0.9
-1.2
-1.5
-1.8
-2.1
-2.4
-2.7
-3.0
-3.3
-3.6
Log Normality - Sodium Oleate
20
30
40
50
60
70
80
90
Equivalent Conductance (Mhos)

Table V

The Increments of Equivalent Conductance of Sodium Oleate Solutions Due to a Surface Layer of Benzene for 23 hours at 25°C.

Normality	Log Normality	Initial Conductance	Final Conductance	Increment
.0608	-1.216	26.89	27.29	.40
.0304	-1.517	28.85	30.07	1.22
.0152	-1.818	32.85	37.22	4.37
.0076	-2.119	38.81	53.53	14.72
.0038	-2.420	49.16	73.14	23.98
.0019	-2.721	59.16	82.99	23.83
.00095	-3.022	73.21	86.95	13.74
.0005	-3.323	73.48	87.37	13.89

Controls of benzene layered on dilute sodium hydroxide were treated in the same way in order to determine the experimental error. Organic acids or bases dissolved in the benzene could bring about increments of conductance. Carbon dioxide, also could if dissolved by the alkali, appreciably change the conductance. The controls exhibited a two per cent decrease in equivalent conductance.

These data are plotted (Fig. 7). Both the graph and the tabulated data emphasize strongly the fact that at 0.002 normal there is an abrupt change in the increments of conductance or observed adsorption. Observed adsorption is a maximum at that concentration and gradually decreases with increasing concentration. On the inferior side of 0.0002 normal the observed adsorption drops abruptly about one-half instead of further increasing.

The interfacial activities of different oils were investigated. The interfacial area was the same as in the previous experiments, namely the liquid/liquid surface formed in the conductivity cell. Aliquot portions of a 0.0118 normal sodium oleate solution were used for each oil.

The different capacities of the various oils to promote interfacial adsorption at the oil/solution boundary were determined by the same method employed in the previous experiments. In these experiments the concentration of sodium oleate and the interfacial area were held constant and the oil was varied. Controls consisting of each oil on dilute sodium hydroxide were again used as checks.

The percentage shifts in conductance with time are tabulated (Table VI) and plotted (Fig. 8).

FIGURE 8

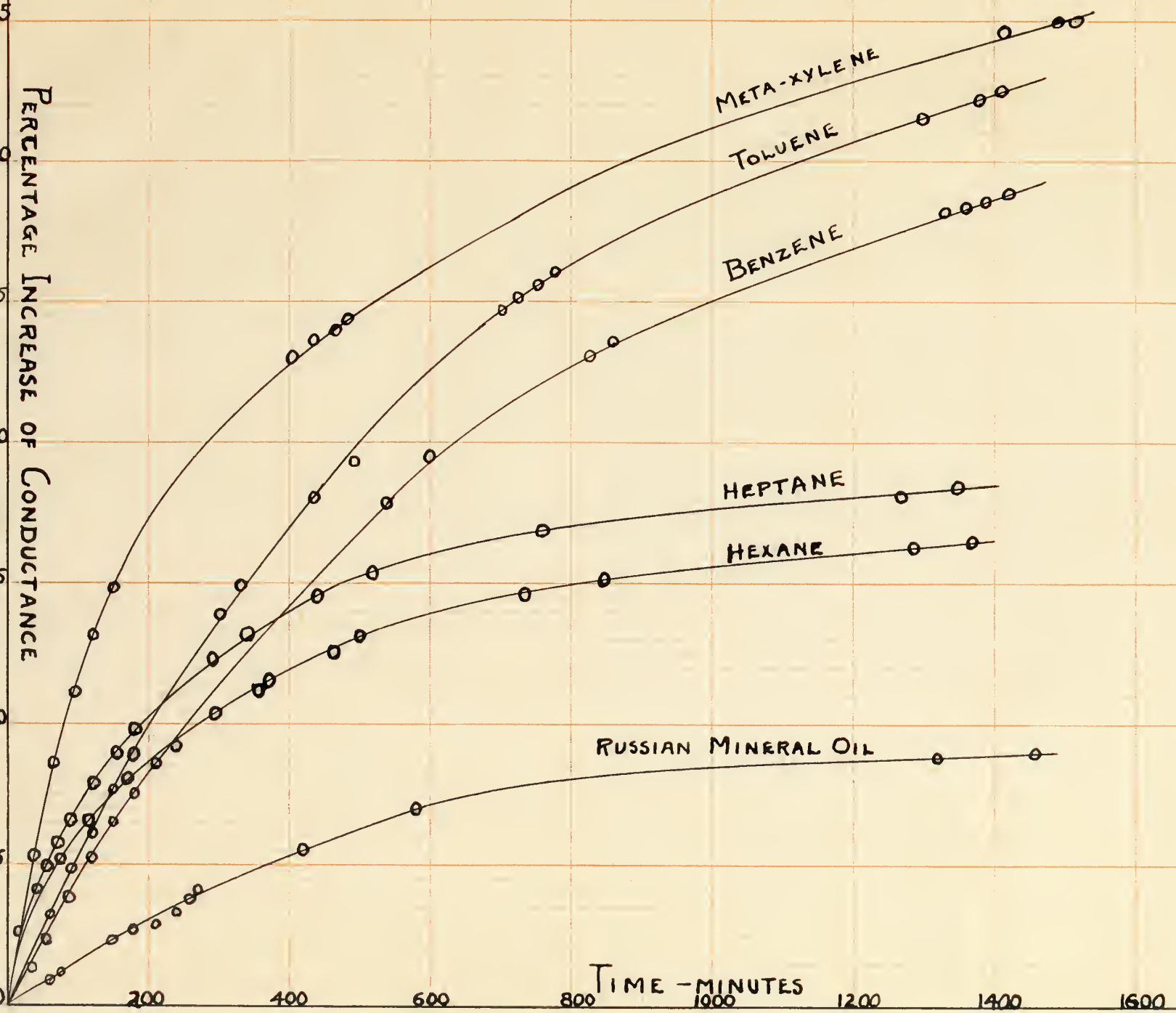

META-XYLENE
TOLUENE
BENZENE
HEPTANE
HEXANE
RUSSIAN MINERAL OIL
PERCENTAGE INCREASE OF CONDUCTANCE
TIME - MINUTES
0
5
10
15
20
25
30
35
200
400
600
800
1000
1200
1400
1600

Table VI

The Percentage Increases of Equivalent Conductance of Sodium Oleate Solutions with Time at 25°C.

(a) When a .0118 normal solution is in contact with a layer of benzene

Time (Minutes)	Equivalent Conductance	Δ Equivalent Conductance	Percentage Increase
0	32.47	0	0
5	32.54	.07	.22
10	32.62	.15	.46
20	32.72	.25	.77
35	32.89	.42	1.29
55	33.24	.77	2.37
90	33.71	1.24	3.82
120	34.18	1.71	5.26
150	34.60	2.13	6.55
180	34.92	2.45	7.55
210	35.26	2.79	8.58
230	35.51	3.04	9.35
540	38.27	5.80	17.85
570	38.51	6.04	18.60
600	38.79	6.32	19.45
830	39.97	7.50	23.08
860	40.13	7.66	23.60
1330	41.63	9.16	28.20
1360	41.68	9.21	28.30
1390	41.76	9.29	28.60
1420	41.82	9.35	28.80

Table VI (Con't.)

(b) When a .0118 normal solution is in contact with a layer of toluene

Time (Minutes)	Equivalent Conductance	Δ Equivalent Conductance	Percentage Increase
0	32.52	0	0
3	32.54	.02	.06
13	32.68	.16	.49
33	33.07	.55	1.7
60	33.56	1.04	3.2
90	34.09	1.57	4.85
120	34.52	2.00	6.15
150	35.01	2.49	7.7
180	35.42	2.90	8.93
210	35.76	3.24	9.6
240	36.15	3.63	11.2
270	36.38	3.86	11.9
300	37.04	4.52	13.9
330	37.35	4.83	14.9
435	38.38	5.86	18.0
495	38.79	6.27	19.3
705	40.51	7.99	24.6
725	40.67	8.15	25.1
755	40.85	8.33	25.6
780	40.99	8.47	26.1
1298	42.76	10.24	31.5
1380	42.99	10.47	32.2
1410	43.08	10.56	32.5

Table VI (Con't.)

(c) When a .0118 normal solution is in contact with a layer of meta xylene.

Time (Minutes)	Equivalent Conductance	Δ Equivalent Conductance	Percentage Increase
0	32.42	0	0
5	32.62	.20	.62
15	33.25	.83	2.56
35	34.13	1.71	5.28
65	35.18	2.76	8.52
95	36.03	3.61	11.15
120	36.65	4.23	13.08
150	37.20	4.78	14.78
405	39.89	7.47	23.02
435	40.09	7.67	23.63
465	40.15	7.73	23.87
480	40.29	7.87	24.30
1415	43.64	11.22	34.6
1490	43.73	11.31	34.9
1515	43.76	11.34	35.0

(d) When a .0118 normal solution is in contact with a layer of heptane.

Time (Minutes)	Equivalent Conductance	Δ Equivalent Conductance	Percentage Increase
0	32.47	0	0
5	32.70	.23	.71
16	33.07	.60	1.85
25	33.34	.87	2.68
40	33.79	1.32	4.06
55	34.08	1.61	4.95
70	34.34	1.87	5.75
90	34.60	2.13	6.55
120	35.02	2.55	7.85
155	35.38	2.91	8.95
180	35.65	3.18	9.78
225	36.03	3.56	10.96
290	36.45	3.98	12.25
340	36.75	4.28	13.20
440	37.22	4.75	14.62
515	37.48	5.01	15.42
760	37.97	5.50	16.93
1265	38.42	5.95	18.31
1350	38.46	5.99	18.45

Table VI (Con't)

(e) When a .0118 normal solution is in contact with a layer of hexane.

Time (Minutes)	Equivalent Conductance	Δ Equivalent Conductance	Percentage Increase
0	32.47	0	0
5	32.63	.16	.49
10	32.82	.35	1.08
15	33.10	.63	1.94
25	33.34	.87	2.68
45	33.70	1.23	3.78
55	33.84	1.37	4.22
75	34.17	1.70	5.23
85	34.24	1.77	5.45
115	34.61	2.14	6.58
145	34.89	2.42	7.45
175	35.10	2.63	8.09
205	35.25	2.79	8.58
235	35.48	3.01	9.26
295	35.81	3.34	10.28
355	36.12	3.65	11.23
375	36.24	3.77	11.60
465	36.54	4.07	12.53
500	36.71	4.24	13.07
735	37.22	4.75	14.62
848	37.38	4.91	15.11
1285	37.77	5.30	16.31
1370	37.81	5.34	16.44

(f) When a .0118 normal solution is in contact with "Puretest" Russian mineral oil.

Time (Minutes)	Equivalent Conductance	Δ Equivalent Conductance	Percentage Increase
0	32.43	0	0
5	32.43	0	0
15	32.47	.04	.12
27	32.53	.10	.31
44	32.63	.20	.62
60	32.73	.30	.92
75	32.82	.39	1.20
150	33.18	.75	2.31
180	33.28	.85	2.62
210	33.36	.93	2.86
240	33.49	1.06	3.26
262	33.65	1.22	3.76
292	33.79	1.36	4.18
420	34.21	1.78	5.48
582	34.67	2.24	6.90
1320	35.27	2.84	8.75
1460	35.34	2.91	8.95

Table VI (Con't)

(g) Controls. The various oils in contact with .001 normal sodium hydroxide.

Time (Hours)	Equivalent Conductance	Δ Equivalent Conductance	Percentage Increase
	Benzene		
0	216	0	0
3 1/2	214	-2	-.84
19	210	-6	-2.55
45	208	-8	-3.38
	Toluene		
0	199.5	0	0
4 1/2	197.4	-2.1	-1.0
20 1/2	196.5	-3.0	-1.5
28 1/2	195.5	-4.0	-2.0
	Meta xylene		
0	189.9	0	0
4 1/2	184.0	-5.9	-3.1
19 1/2	182.0	-7.9	-4.2
26	181.0	-8.9	-4.7
	Heptane		
0	189.9	0	0
3	187.1	-2.8	-1.47
5 1/2	187.1	-2.8	-1.47
20	185.2	-4.7	-2.5
	Hexane		
0	184.4	0	0
6 1/2	181.7	-2.7	-1.47
24	180	-4.4	-2.4

It should be observed that the controls show negative shifts with respect to the positive increments of conductance for sodium oleate. The results for sodium oleate must, therefore, be slightly low.

The conditions imposed for the third aspect of the interfacial investigation required that the oil and the concentration of the sodium oleate solution be kept the same as the interfacial area was varied.

The method employed in this series of experiments was slightly different from the foregoing. A series of Pyrex vessels which gave progressively larger interfacial areas with the same volumes of oil and sodium oleate solution were fitted with short glass tubes of medium diameter. Twenty-five cubic centimeters of the soap solution were placed in each vessel. Subsequently 25 cubic centimeters of oil were layered on the solution in each vessel. The short glass tubes afforded a means of removing an aliquot of the aqueous layer without oil contamination.

Measurements were recorded after the oils and solutions had stood in contact for various time intervals. A 10 cubic centimeter pipette was inserted into the aqueous layer through the glass tube. An oil-free aliquot was thus removed and placed in the dry conductivity cell. The reading was taken immediately. It was observed that the conductance was changing slightly with time.

Approximations of the interfacial areas were calculated from the diameters of the vessels at heights of the interfaces in the containers.

The graph (Fig. 9) represents the conductance-recorded adsorption by the interface when all factors were constant except the area. The data have been tabulated (Table VII).

Table VII

The Effect of Interfacial Area Variation on the Equivalent Conductance of Sodium Oleate Solutions at 25°C.

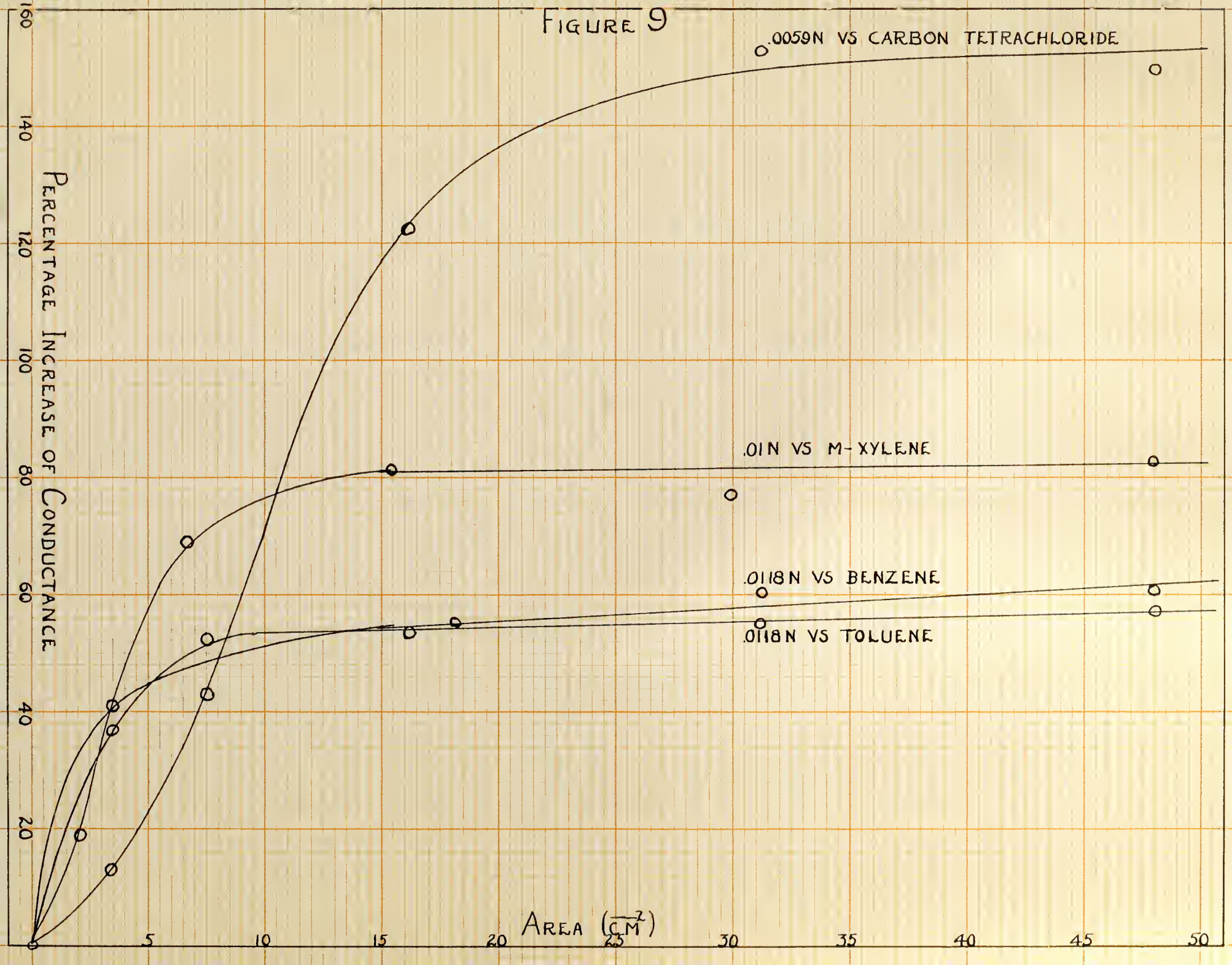
Area (cm^{-2})	Equivalent Conductance	Percentage Increase	Oil	Concentration of Solution
vapor	33.04	0	Benzene	.0118 normal
3.45	46.51	40.8	"	" "
18.1	51.55	55.1	"	" "
31.2	53.00	60.5	"	" "
47.8	53.04	60.6	"	" "
vapor	33.45	0	Toluene	.0118 normal
3.45	45.72	36.7	"	" "
7.54	51.10	52.6	"	" "
16.15	51.3	53.3	"	" "
31.2	51.88	55.0	"	" "
47.8	52.70	57.5	"	" "
vapor	40.85	0	Carbon	
3.45	46.02	12.6	tetrachloride	.0059 normal
7.55	58.28	42.5	"	" "
16.15	90.82	122.0	"	" "
31.2	103.3	153.0	"	" "
47.8	102.2	150.0	"	" "
vapor	36.36	0	M-xylene	.01 normal
2.17	42.96	18.2	"	" "
6.58	61.33	68.7	"	" "
15.35	65.89	81.2	"	" "
29.8	64.34	77.0	"	" "
47.8	66.60	83.0	"	" "

The values for carbon tetrachloride which are reproduced in the graph (Fig. 9) have an additional interesting feature. Carbon tetrachloride has a greater density than the sodium oleate solution, and hence sinks to the bottom of the container. The adsorption which ensued with time took place at the bottom surface of the solution.

The errors involved in transferring aliquots to the cell and in measuring interfacial areas are undoubtedly large. The results reported (Fig. 9) are nevertheless significant because the relative effect of changing interfacial area is positively demonstrated. Just as in the case of varying time intervals (Fig. 8) the conductance-recorded interfacial adsorption with varying areas approaches an asymptotic limit after a rapid initial increase.

It has been noted previously that a portion of the aqueous layer of a two phase oil/solution system undergoes slight changes in conductance when it is removed from the system. It should be recalled also (Fig. 5) that these solutions were more or less turbid originally. When an oil was layered on the surface of one of the less turbid solutions (Fig. 5) the colloidally dispersed acid sodium oleate dissolved slowly and in two or three hours the solution was rendered clear and colorless. The action is identical with the clarification which dilute alkalies brought about in the same solution. If, moreover, the solution were only slightly more concentrated than 0.002 normal, clarification, due to the oil layer, took place more rapidly and a clear aqueous phase resulted. The adsorption did not stop at that point because the aqueous layer again became turbid. The intensity of the turbidity which developed after the clearing phenomenon had taken place was limited by the magnitude of the interfacial area with respect to the volume of the aqueous solution and also, by the concentration of the aqueous sodium oleate phase. Thus, under the same conditions of

FIGURE 9


.0059N VS CARBON TETRACHLORIDE
.01N VS M-XYLENE
.0118N VS BENZENE
.0118N VS TOLUENE
PERCENTAGE INCREASE OF CONDUCTANCE
AREA ($\frac{CM^2}{}$)
160
140
120
100
80
60
40
20
5
10
15
20
25
30
35
40
45
50

interfacial area to volume of aqueous solution, the higher concentrations of sodium oleate manifested only an apparent decrease in the quantity of precipitated acid sodium oleate, the lesser concentrations became quite clear whereas solutions of concentrations just slightly greater than 0.002 normal became clear and then turbid again.

When an oil-free aliquot of a solution with such an oil-induced turbidity was removed and placed in the conductivity cell, the solution again cleared with a slightly changing conductance. A comparison of these effects for a surface and a bottom layer of oil is given in Table VIII.

Table VIII

The Fluctuation of Conductance of Sodium Oleate Solution After Removal from Oil System.

M-xylene (surface layer)		Carbon tetrachloride (bottom layer)	
Time (Minutes)	Resistance (Ohms)	Time (Minutes)	Resistance (Ohms)
0	--	0	--
.75	858.6	1	635.1
1.75	852.8	2	637.8
3.75	849.4	3	640.8
4.75	848.4	4	643.5
5.75	847.7	6	648.6
10	847.0	8	652.8
13	847.7	10	656.4
18	848.4	13	660.0
22	850.1	16	665.4
25	850.4	21	669.3
30	851.1		

These data are characteristic of bottom and surface layers of oil. A portion of the aqueous solution under an oil layer suffers first a fall

in conductance and then rises again as the turbidity disappears. The conductqnce of the aqueous solution removed from above an oil (carbon tetrachloride) rises staadily to a constant value.

A further observation was made in connection with the clarification and reappearance of the turbidity under the influence of a surface layer of oil. In the experiments on interfacial surface variation it was noted that conditions which gave the measurements in the steep portion of the curve (Fig. 9) were characterized also by clear substrata. Solutions which corresponded to the points in the flat portion of the curve were characterized by an oil induced turbidity.

DISCUSSION

It is readily apparent that the material adsorbed at the oil/sodium oleate solution interface is in chemical equilibrium with that dissolved in the aqueous substratum. The conductivity measurements in these adsorption experiments depends upon the free sodium hydroxide produced by hydrolysis of the solute, sodium oleate. Any changes in conductance must record fluctuations in the concentration of sodium hydroxide in the solution because mobilities must be nearly constant in the same solution. It is evident further, that if the equivalent conductance increases as it does in all of these experiments, that the sodium hydroxide content has increased.

(1) $NaOl + H_2O \rightleftharpoons NaOH + \text{Acid } NaOl$

Increases of sodium hydroxide content in these cases are a manifestation of further hydrolysis. The chemical equation given above approximates closely enough the result. By the law of mass action the equilibrium expression of the indicated chemical process can be stated in mathematical form as

(2) $K [NaOl] [H_2O] = [NaOH] [\text{Acid } NaOl]$

in which the brackets are used to denote concentration and K is the equilibrium constant. From the definition of mass action the concentrations involved are those of the molecular equilibrium only. The general expression for the equilibrium constant K is then

(3) $$K = \frac{[NaOH] [\text{Acid } NaOl]}{[NaOl] [H_2O]}$$

When a sodium oleate solution is in equilibrium with its surface and its vapor, the values of $[NaOH]$, $[NaOl]$, and $[\text{Acid } NaOl]$ substituted

in the general equation give a definite constant K. When an oil is layered on the surface of the solution [NaOH] increases. In that particular system [NaOH] increases at the expense of [Na Ol] in the chemical equation (1). The expression for K (3) then becomes

$$(4) \quad K = \frac{[NaOH + \Delta][Acid\ NaOl]}{[NaOl - \Delta]}$$

By comparing equation (1) the initial state of the solution is equilibrium with its saturated surface and vapor, and equation (4) the state of the solution after interfacial adsorption of the acid salt, it becomes evident that Acid NaOl must have decreased to maintain K under the new conditions. The concentration of the acid sodium oleate is lowered by interfacial adsorption. Acid sodium oleate is adsorbed and removed from the chemical equilibrium in the solution.

The deduction that acid sodium oleate is adsorbed at the interface is qualitatively verified in the previous experiments. It has been shown that in the case of the vapor/solution interface the white turbidity is a colloidal dispersion of acid sodium oleate. Dilute alkalies dissolved it. The same process takes place during adsorption at an oil/solution interface. The concentration of the sodium hydroxide increases as recorded by conductivity measurements.

The white, colloidal dispersion of acid sodium oleate cannot be considered a part of the molecular equilibrium. If, then, it is adsorbed the concentration of sodium hydroxide cannot increase until all of the colloidal excess of acid sodium oleate has been removed. The adsorption of more acid sodium oleate than exists as a colloidal dispersion causes the equilibrium to shift and as a result the equivalent conductance of the solution increases. Hence the colloidally dispersed material is in equilibrium with the molecular dispersion.

Increments of conductance are manifestations of the removal of the colloidal excess and shifts in the molecular equilibrium. In the light of this statement the so-called conductance recorded adsorption from solutions of varying concentrations (Fig. 7) is readily interpreted. In the case of the greatest concentration the conductance does not increase when benzene is layered on the solution. The increments of conductance are then progressively larger for the lesser concentrated solutions and reach a maximum at 0.002 normal. The maximum increase is coincident with the clear solution 0.002 normal as would be expected.

The interface vapor/solution is saturated in the case of solutions 0.002 normal and greater. The result, therefore, of acid sodium oleate adsorption by the oil/solution interface is the substitution of acid sodium oleate for the sodium oleate in the surface layer of the aqueous solution. The vapor/solution interfaces of solutions of lesser concentration than 0.002 normal are not saturated hence adsorption goes on normally without substitution.

In contact with the vapor a saturated sodium oleate interface is in dynamic equilibrium with the main portion of the solution. It has already been shown that the molecular hydrolytic system in the solution is in equilibrium with the colloidal dispersion. The whole system may be visualized as

saturated Surface solute <------> saturated Molecular solute <------> Colloidal excess

If the solution is shaken a stable foam is generated. The solute in the surface foam is not rapidly removed to satisfy the constant K because it is not necessary. Stable foams are a characteristic of those solutions which have a saturated surface and a colloidal excess in dynamic relationship with a molecular equilibrium.

The clear solution in the series of sodium oleate solutions (Fig. 5) has the minimum surface tension (Fig. 4). The clarity of the solution 0.002 normal must indicate that all of the insoluble colloidal excess is in solution or is adsorbed at the vapor/solution interface. In either case there must be proportionally more acid sodium oleate in the surface than there is in the surfaces of turbid solutions. That conclusion leads directly to the deduction that acid sodium oleate lowers the surface tension to a greater extent than does sodium oleate. Because sodium oleate has the maximum amount of sodium in its chemical combination its solubility is greater than that of acid sodium oleate which has fewer sodium atoms to the same number of oleic acid nucleii. From the standpoint of the interface the more soluble sodium oleate will tend to enter the main body of the solution and the less soluble acid sodium oleate will tend to escape from the main body. The less soluble material exhibits the greater tendency to lower the surface tension of water.

A further complicating factor is introduced by the particular oil which is inducing the adsorption of acid sodium oleate. The graph (Fig.8) not only illustrates the effects of different oils under the same conditions of adsorption but also makes necessary the deduction that each oil is characterized by a specific capacity to promote hydrolysis. Benzene, toluene and meta-xylene exhibit progressively greater powers of removing acid sodium oleate. The chain hydrocarbons hexane and heptane are similar to each other in their effects.

The analysis of these curves in terms of the equilibrium equation

$$(3)\quad K = \frac{[NaOH]\,[\text{Acid NaOl}]}{[NaOl]}$$

and free interfacial energy necessitates the use of the expression alkali tolerance. It is very evident that the meta-xylene interface

adsorbs acid sodium oleate and strongly distorts the normal equilibrium (eq. 1) notwithstanding an increasingly greater quantity of free sodium hydroxide. As the equilibrium is distorted the sodium hydroxide must tend more and more to suppress hydrolysis and neutralize the acid soap which is present. In the case, then, of meta-xylene the interfacial forces which promote adsorption must be enormous in order to distort the equilibrium as they do. The interfacial forces of adsorption are identical with the interfacial free energy of the thermodynamics of surfaces. The capacity of a particular oil to distort the molecular equilibrium or to induce further hydrolysis in spite of a growing suppression tendency as a result of its interfacial activity, is an alkali tolerance. The free energy of an interface must be a direct function of alkali tolerance. The graph indicates, therefore, that the lower alkali tolerances of hexane and heptane are due to lower interfacial free energies for these oils.

The experiments concerning the interfacial area variation lead to an extremely important result. The graphical representation of the data (Fig. 9) shows that a small but increasing interfacial area induces more and more hydrolysis. Eventually the curve becomes flat, a condition which indicates that the maximum alkali tolerance has been reached. No further hydrolysis takes place to any extent but the aqueous substratum becomes turbid again after passing through the clear zone of the steep portion of the curve. The equilibrium equation

$$(3) \quad K = \frac{[NaOH]\,[\text{Acid} \overset{\text{Colloidal excess}}{\downarrow\uparrow} NaOl]}{[NaOl]}$$

again suggests the explanation. If the equation (3) expresses the conditions in the vapor/solution system then the creation of an oil/solution interface at maximum alkali tolerance becomes

$$(5)\quad K = \frac{[NaOH + \Delta\,max][Acid\ NaOl]}{[NaOl - \Delta\,max]}$$

The interfacial area is further increased and consequently the free interfacial energy increases. In order to offset the increased free energy a further distribution of solute takes place between the aqueous layer and the interface. Acid sodium oleate has been removed already to the maximum hence sodium oleate the only other adsorbable component of the system concentrates at the interface. The quantity of dissolved sodium oleate suffers a further change of ϕ the amount adsorbed as sodium oleate and leaves the dissolved concentration $[Na\ Ol - \Delta\,max - \phi]$. The $[NaOH + \Delta\,max]$ does not change hence $[Acid\ Na\ Ol]$ must decrease by ψ to satisfy the equilibrium conditions. If it is assumed that the final concentration of acid sodium oleate becomes $[Acid\ Na\ Ol - \psi - \theta]$ the mathematical expression which results is

$$(6)\quad K = \left[\frac{NaOH + \Delta\,max}{NaOl - \Delta\,max - \phi}\right][Acid\ NaOl - \psi - \theta]$$

θ colloidal

The quantity θ is the acid sodium oleate which must leave the molecular equilibrium when the quantity of sodium oleate is decreased by ϕ. The decrease of θ in the solution takes place by the formation of a colloidal excess and the solution becomes turbid again.

The effect of clarifying and subsequently re-inducing a colloidal precipitate as caused by oils is similar to the photograph (Fig. 5). The initial sodium oleate solution is turbid like, for example, the .0076 normal solution in the photograph. After the oil has been layered on the surface of that solution the turbidity slowly disappears and the aqueous solution then is clear like the .0019 normal tube. As adsorption proceeds further, however, the aqueous layer becomes turbid again similar to the 0.00095 normal solution. Note should be made of the fact that when an oil

has caused a solution to clear the visible conditions in the solution are similar to those which exist at 0.0019 normal (Fig. 5).

The observation has already been reported that a portion of a turbid aqueous solution, which has been cleared and rendered turbid again by an oil interface, undergoes rapid clarification when removed from contact with the oil. Conductance data (Table VI) show that the loss of turbidity is coincident with changes in the equilibrium particularly in the free sodium hydroxide. In the case of the meta-xylene a fresh vapor/solution interface is created when a portion of the aqueous substratum is removed, but in the case of the carbon tetrachloride no new vapor/solution interface is formed in the removal. In both cases, however, new glass/solution interfaces are formed hence the conductance data are subjected to an influence of unknown magnitude. Nevertheless the data do show that the formation of a fresh surface causes first a small increase in the concentration and then a decrease to a constant value. Regardless of conductance changes it is apparent that the formation of fresh interfaces, vapor/solution and solution/glass, are followed by the concentration of the acid sodium oleate at these new free energy regions.

It is entirely possible that the surface concentration of acid sodium oleate may be the mechanism by which the colloidal acid sodium oleate is formed. It has already been demonstrated that the presence of a maximum quantity of acid sodium oleate in the surface layer is coincident with the minimum surface tension. In addition acid sodium oleate has been shown both theoretically and experimentally to possess the highest escaping tendency and is, therefore, the most easily adsorbed component.

A freshly formed surface may first take up acid sodium oleate. In this process the surface tension decreases as many investigators have already observed. When the surface becomes saturated with acid sodium

oleate, the surface tension becomes a minimum. If now, more acid sodium oleate goes into the surface layer, the surface area must increase to make room for this excess. Under these conditions increases of the area of the surface would result in the formation of a wrinkled or rugose layer. As this wrinkling effect becomes accentuated more and more by the adsorption process, a condition is ultimately attained in which nodules of the surface layer may detach themselves in much the same manner as a drop of liquid slowly forms on a tip and falls as a sphere. The detached nodules are then colloidal aggregates of acid sodium oleate. This mechanism is borne out by two facts. First, after reaching a minimum, the surface tension of a fresh solution increases again to a constant value, a fact which indicates the gradual loss of acid sodium oleate from the surface. Second, the formation of the colloidal acid sodium oleate is hastened by a fluctuating temperature. Obviously, the expansion and contraction as well as the changes in solubility with temperature could assist such a mechanism.

If the surface layer of molecules is oriented according to Harkins' and Langmuir's theory, the colloidal particles of acid sodium oleate formed by the process just outlined must bear out the multivalent ion theory. The surface is assumed to have the soluble sodium ends of the adsorbed molecules dipping into the aqueous layer, and the insoluble oleic acid ends of the molecules projecting into the vapor. A colloidal particle formed after the manner of a detached drop will then have the sodium ends of the molecules on the outside and the oleic acid chains dipping into each other.

Further Discussion of the Literature

Mikumo (46) attributed the influence of sodium hydroxide on soap solutions to a peptizing action. Such an explanation is vague. It is probable that the effect of sodium hydroxide is to suppress hydrolysis, at least in the dilute solutions, and form more of the neutral soap from the acid product.

The failure of Ettisch and Koganei (16) to observe a minimum in the surface tension-concentration curve of sodium oleate invalidates their other data. The numerous reports of the minimum effect in the case of sodium oleate by other investigators substantiates the existence of the phenomenon.

The mechanism suggested by Pickering (51) to explain the stability of oil droplets in soap solutions is impossible. The present investigation proves conclusively that the film is not formed from solid particles but rather is formed by adsorption from the molecular equilibrium. The incidental disappearance of the colloidal particles as the equilibrium shifts has been shown to influence the conductivity of the solution. On the contrary the direct adsorption of solid particles would not change the conductance.

The rate-curves of adsorption which takes place from these soap solutions are similar to the parabolic rate function reported by Nugent (49). The rate at which acid sodium oleate is adsorbed is determined also by the instantly available quantity, the solubility, as well as by the velocity of diffusion. The low solubility of the acid salt justifies the previous criticism of Shorter's work (60) with the Donnan pipette. Shorter concluded that acid soap was not surface active. Instantaneous measurements such as those obtained with the Donnan pipette could lead to this erroneous

conclusion. It has been shown in the present investigation that acid sodium oleate is extremely surface active.

Clayton (8) makes the obscure statement that "possibly the difficultly-soluble acid sodium oleate produced by hydrolysis may be a factor in emulsification". The present investigation shows that unquestionably acid sodium oleate is the first material adsorbed. In addition, its function in emulsification is obviously determined by the amount present whether molecularly dispersed or in colloidal suspension.

Briggs' (5) adsorption data which were obtained by titration of a system in equilibrium are subject to the criticism that the differences of concentration of sodium in the aqueous phase are <u>not</u> a criterion of the sodium oleate adsorbed.

The theory of selective adsorption of specific ions which has been suggested by Vincent (64) must be modified. If only oleate <u>ions</u> were adsorbed as this theory requires, then the sodium ions remaining in solution could not conduct electricity. If such were the case, the conductance would decrease. On the contrary, this investigation demonstrates that the conductance increases and is due to sodium hydroxide. The criticism by Rhodes and Bascom (57) is, therefore, sustained.

Fischer and Harkins' (18) statement that oil droplets enveloped in condensed films of sodium oleate are more stable than those in expanded films is not clear. It is true, however, that acid sodium oleate molecules will reside deeper in the interface than will sodium oleate molecules because the former are less soluble in water than the latter.

The nature of the conductivity data resulting from this investigation makes the quantitative consideration of Gibbs' adsorption equation almost impossible. However, there is, at least, one consideration of major importance which has been clarified, the preferential adsorption of acid

sodium oleate at oil/solution interfaces. The concentration of the acid salt is exactly what is to be expected from its composition.

It has been shown that the turbidity in these solutions is a colloidal dispersion of acid sodium oleate. It has been shown also that with decreasing concentration the turbidity gradually becomes less and that, at 0.002 normal, the acid soap is completely dissolved in the interfaces. The surface energy is a minimum at 0.002 normal, Obviously, conditions under which the concentration of acid sodium oleate in the interfaces is maximum,are those of minimum free interfacial energy and of the absence of a turbidity.

The clarification which takes place when an oil is layered on a turbid solution must be subject to the same conditions. The aqueous solution clears and becomes turbid again as the conductance increases and becomes constant. Thus, in any case,the interfacial energy is a minimum when the substratum is clear. The quantity of acid sodium oleate adsorbed is determined by the available quantity. The latter is conditioned by the concentration of the solution in which the acid sodium oleate is suspended.

The crystalline deposit of acid sodium oleate which forms in the sodium oleate solutions of higher concentration precludes a molecular dispersion of the acid salt because crystallization of the colloidal material is inconceivable. Interffacial adsorption must, therefore, be a molecular phenomenon.

In every case those solutions of sodium oleate which produced stable foams were characterized by a molecular hydrolytic system in equilibrium with both a colloidal excess of solute and an interface saturated with solute.

These observations show that interfacial adsorption is conditioned by the molecular equilibrium in the aqueous solution. The formation under

these conditions of an oriented surface layer is not only conceivable but necessary. An oil droplet which suffers adsorption of this kind will ultimately be encased in oriented solute molecules. The hydrocarbon oleate chain will reside in the oil because it has a high fugacity from the polarized aqueous medium. The highly polar sodium ends of the chains will reside in the water. The oil droplet then satisfies the requirements of the multi-valent ion theory both as to charge and as to the sign of that charge.

CONCLUSIONS

The adsorption of sodium oleate at the interfaces between oils and solutions of this salt has been investigated frequently because it constitutes a comparatively simple case of the general colloidal phenomenon. In addition, it has been studied to elucidate the general behavior of soaps in the light of their practical usefulness. Theories of adsorption which arise from investigations of the first type may be interpreted both for the accurate resolution of complex colloidal phenomena, and for the clearer understanding of the action of soaps in practice.

The general problem of adsorption was formulated by Gibbs, who evaluated mathematically the thermodynamic surface relationships. It has long been known that Gibbs' equations are only qualitatively correct for soap solutions because the assumptions involved do not extend to colloidal systems like the latter.

The conductivity method of determining adsorption has been employed in this investigation because it has several distinctive advantages. In the first place, it makes possible the determination of adsorption without the introduction of such errors as those which arise when the equilibrium system is titrated. In the second place, the method measures the progress of adsorption without distortion of the equilibrium. Finally, the active surface can be measured with sufficient accuracy to insure conclusive results.

The conductivity data demonstrate conclusively that the adsorbed material is in equilibrium with that dissolved. The mechanism by which interfacial adsorption takes place is conditioned largely by the concentration of the sodium oleate solution from which adsorption removes solute.

Detergency is a characteristic of those solutions of sodium oleate in which a molecular hydrolytic system is in equilibrium with both saturated interfaces and an excess either colloidal or colloidal and crystalloidal.

Adsorption removes solute from that which is molecularly dispersed. Adsorption of the colloidally suspended material is, therefore, an indirect process which depends upon an equilibrium between the molecularly dissolved and the colloidally dispersed material.

The first component adsorbed from the hydrolytic system sodium oleate-water-sodium hydroxide-acid sodium oleate is the least soluble; that is, acid sodium oleate. The adsorption of this component proceeds according to the laws of Mass Action. The excess of sodium hydroxide, due to the equilibrium shift as acid sodium oleate is adsorbed, finally suppresses further hydrolysis of the sodium oleate. Further adsorption removes molecular sodium oleate.

Different oils possess differing capacities to shift the hydrolytic equilibrium. The free alkali which arises from the distortion of the equilibrium is a measure of the interfacial free energy. It has been called the alkali tolerance of the oil interface.

The same reactions are true of both surface and bottom interfaces and, therefore, must apply to intermediate interfaces - those around suspended oil droplets.

The mechanism of interfacial adsorption, which this investigation defines in the case of sodium oleate solutions, supports the consideration of oil-in-water emulsions as examples of the type to which the multivalent ion theory of colloids applies.

The interfacial free energy is a minimum under conditions of the maximum adsorption of acid sodium oleate.

The mechanism by which colloidal acid sodium oleate is formed appears to be a surface phenomenon. The colloidal particles may result from further adsorption beyond saturation in the surface layer.

SUMMARY

1. Conductimetric methods have been successfully employed in the investigation of surface phenomena.

2. The surface tension of sodium oleate solutions is an inverse function of hydrolysis in the higher concentrations.

3. Several properties of sodium oleate solutions change abruptly at 0.002 normal, namely surface tension, foaming power, turbidity and equivalent conductance.

4. The conductivity data show that the colloidal acid sodium oleate is in equilibrium with a molecular hydrolytic system.

5. Foams are stable on those sodium oleate solutions which are characterized by a saturated surface layer and a colloidal excess in equilibrium wwith a molecular, hydrolytic system.

6. The maximum concentration of acid sodium oleate in the surface layer is coincident with a minimum surface tension.

7. The higher fugacity of acid sodium oleate causes it to be adsorbed first.

8. The adsorption of sodium oleate takes place after the hydrolytic equilibrium has suffered the maximum distortion through the removal of acid sodium oleate.

9. Various oils exhibit different capacities to adsorb acid sodium oleate.

10. More acid sodium oleate is adsorbed at the oil/solution interface than at the vapor/solution boundary of the same sodium oleate solution.

11. Adsorption from the colloidal phase in sodium oleate solutions takes place indirectly through the molecular equilibrium.

12. The law of mass action explains the activity of dilute sodium oleate solutions.

13. A theory has been suggested to explain the formation of colloidal acid sodium oleate.

14. The multi-valent ion theory of colloidal surfaces has been used to visualize the oil/sodium oleate solution interfaces.

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